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DEVELOPMENT AND CHARACTERIZATION OF SELECTED SYNTHESIS CATALYSTS

DSS Contract No. 37ST.23440-5-9088

Report Submitted by:

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SUMMARY

This report contains the details of the methods of preparation of the following eight catalysts:

1. Iron/alumina
2. Iron/silica
3. Iron/titania
4. Iron/zirconia
5. Nickel/alumina
6. Nickel/silica
7. Nickel/titania
8. Nickel/zirconia

All the catalysts were prepared by the method of impregnation. The chemicals used were of the highest purity available.

In this report all the pertinent information for a given catalyst has been compiled and presented under that particular catalyst. This way each 'catalyst preparation section' is complete by itself.

A number of problems had to be overcome during the preparation of these catalysts. These have been described and discussed under the 'General Comments'.

SOMMAIRE

Ce rapport contient les details des methodes de preparation pour les huit catalyseurs suivants.

1. fer/alumina
2. fer/ silica
3. fer/titania
4. fer/zirconia
5. nickel/alumina
6. nickel/silica
7. nickel/titania
8. nickel/zirconia

Tous les catalyseurs ont ete prepares par la methode d'impregnation. Les produits chimiques utilises etaient les plus purs possible.

Dans ce rapport, toute information pertinente pur chaque catalyseur est compilee et presentee. En utilisant cette methode, chaque "catalyst preparation section" est complete en elle-meme.

Les problemes survenus, lors de la preparation de ces catalyseurs sont decrits et discutes dans la section: "General Comments".

PREPARATION OF IRON/ALUMINA CATALYST

1. Chemicals and Supports

(i) Iron Nitrate

Formula: $Fe(NO_3)_3 \cdot 9\ H_2O$

Supplier: B.D.H. Chemicals Canada
15, 501 - 45th Street West
Saskatoon, Sask. S7L 5Z9

Description: 'ANALAR' Analytical reagent grade
Pale mauve crystals
Minimum assay: 98.5%

Maximum Limits of Impurities	wt %
Insoluble Matter	.003
Free Acid (HNO_3)	.4
Chloride	.005
Phosphate	.004
Sulphate	.005
Calcium	.005
Copper	.005
Ferrous Ion	.002
Lead	.008
Magnesium	.003
Manganese	.005
Potassium	.02
Sodium	.01
Zinc	.01
Total (excluding Free Acid)	.0805
Maximum metal impurities	.066

This grade is the highest purity offered by B.D.H.

(ii) Alumina

Formula: Al_2O_3

Supplier: Kaiser Chemicals
Box 1031
Baton Rouge, LA. 70821

Description: Versal GH (gamma phase)
High density
Surface area: 300 m^2/g
Density: 350 g/L

Impurities	wt %
Na	.005
Fe	.023
Cl	.024
Si	.04

The analysis does not give the absolute purity of alumina, but only the level of impurities with the inference that the balance is alumina. A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the support: The following were measured in our laboratory.

1. BET Area: $278 \pm 2 m^2/g$

2. Pore volume distribution: See Fig. 1

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of alumina was placed in a large stainless steel bowl and dried in a Blue M-Convection oven at 150°C for 24 h. We used two bowls: one contained 982.5 g of alumina (Batch A), and the second contained 1138.2 g (Batch B).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Fe on Alumina support, 374.3 g of iron nitrate was dissolved in 1178 mL of distilled water and the resulting solution slowly poured over the alumina support with gentle and even mixing. This mixing was continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation.

(b) Impregnation of Batch B: For this batch, we dissolved 433.5 g of iron nitrate in 1368 mL of the distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The bowls containing the catalyst paste (resulting from the impregnation step (ii) were placed in the Blue M-Convection oven to dry at 90°C for 24 h. Care was taken to spread around the catalyst paste in the bowl for ease in drying. Also, the bowls were covered with stainless steel (SS) sheets (with a number of holes for the moisture to escape) to ensure that no catalyst was lost by convection currents in the oven.

(iv) Calcination of the Catalyst

The dried catalyst was transferred from the stainless steel bowls to procelain bowls for the calcination step. Again, the bowls were covered with stainless steel sheets with holes. These bowls were now placed in the oven and the oven temperature increased to 450°c (it took about 1 h to attain this temperature). Calcination was continued at 450°c for an additional 24 h. The oven was then turned off. When the oven temperature reached 200°c (30 min), the bowls were removed from the oven and allowed to cool to room temperature.

(v) Chemical Analysis of the Catalyst

Both catalyst Batches A and B were well mixed by putting them together in a ball mill without the balls. The mixing was continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be copleted representative. BET Surface Area measurements were made of both Batches A and B. The Saskatchewan Research Council analyzed the mixed catalyst for Fe determination. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 2.

(vi) Sizing of the Catalyst

(a) Milling

The catalyst was milled in a ball mill down to -100 +200 mesh size. This gave an extremely well-mixed catalyst powder.

(b) -70 +100 Mesh Catalyst Powder

-100 +200 mesh powder was pelletized into 1 1/8" diameter pellets of approximately 7-8 grams each. A pressure of 3000 psig was applied for one minute to make the pellets. The pellets were gently crushed and then sieved for -70 +100 mesh size range.

(c) Pelletizing

-100 +200 mesh powder was mixed with enough stearic acid to give 1 wt % stearic acid in the mixture. To ensure even mixing, the catalyst powder and stearic acid were mixed for 1 h in a ball mill without the balls. The pellets were made with an automatic pelletizing machine using 3 mm dies and punches. (The dies and punches were obtained from Stokes-Merril, 955 Mearns Road, Warminster, Penn. 18974, U.S.A.)

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface area were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. Values obtained are presented in Fig. 2.

(b) Pore Volume Distribution

The pore volume distribution was determined from the Nitrogen desorption isotherm using the above Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Fig. 3.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. These values are given in Fig. 2.

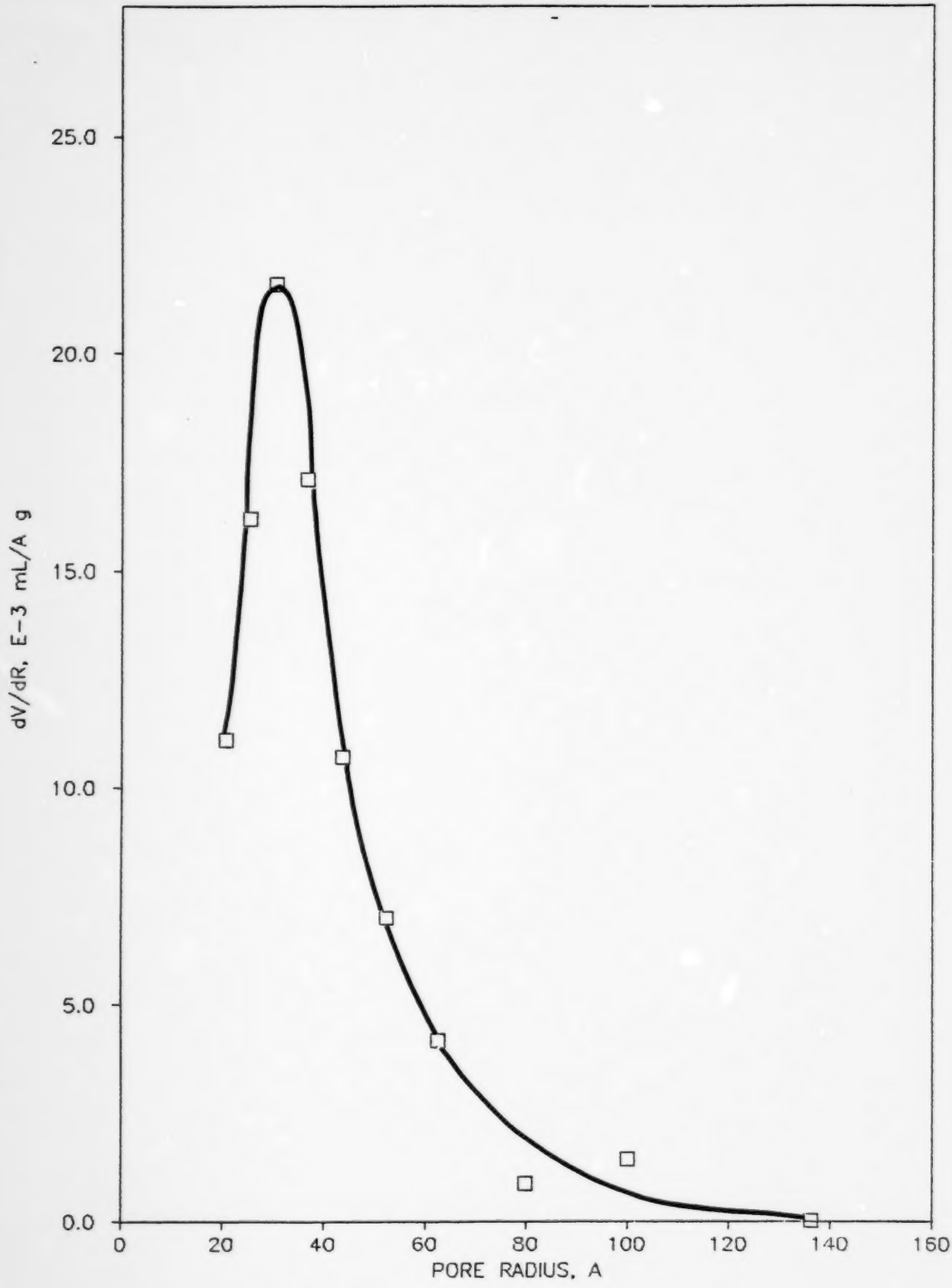

Fig. 1: Pore Volume Distribution of the Alumina Support

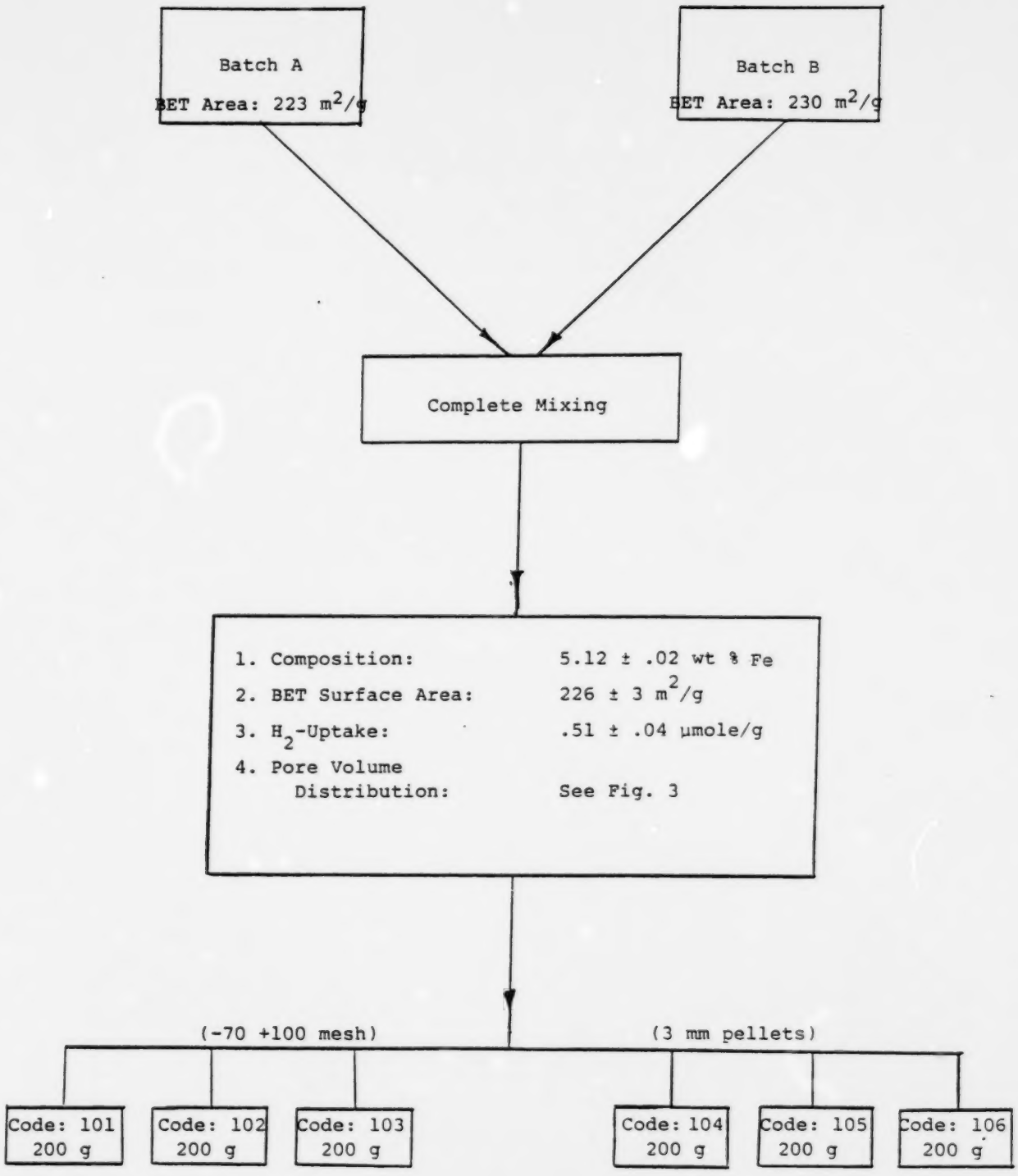
Batch A
BET Area: 223 m²/g
Batch B
BET Area: 230 m²/g
Complete Mixing
1. Composition: 5.12 ± .02 wt % Fe
2. BET Surface Area: 226 ± 3 m²/g
3. H₂-Uptake: .51 ± .04 µmole/g
4. Pore Volume Distribution: See Fig. 3
(-70 +100 mesh)
(3 mm pellets)
Code: 101 200 g
Code: 102 200 g
Code: 103 200 g
Code: 104 200 g
Code: 105 200 g
Code: 106 200 g

Fig. 2 Preparation and Characterization of the Iron/Alumina Catalyst

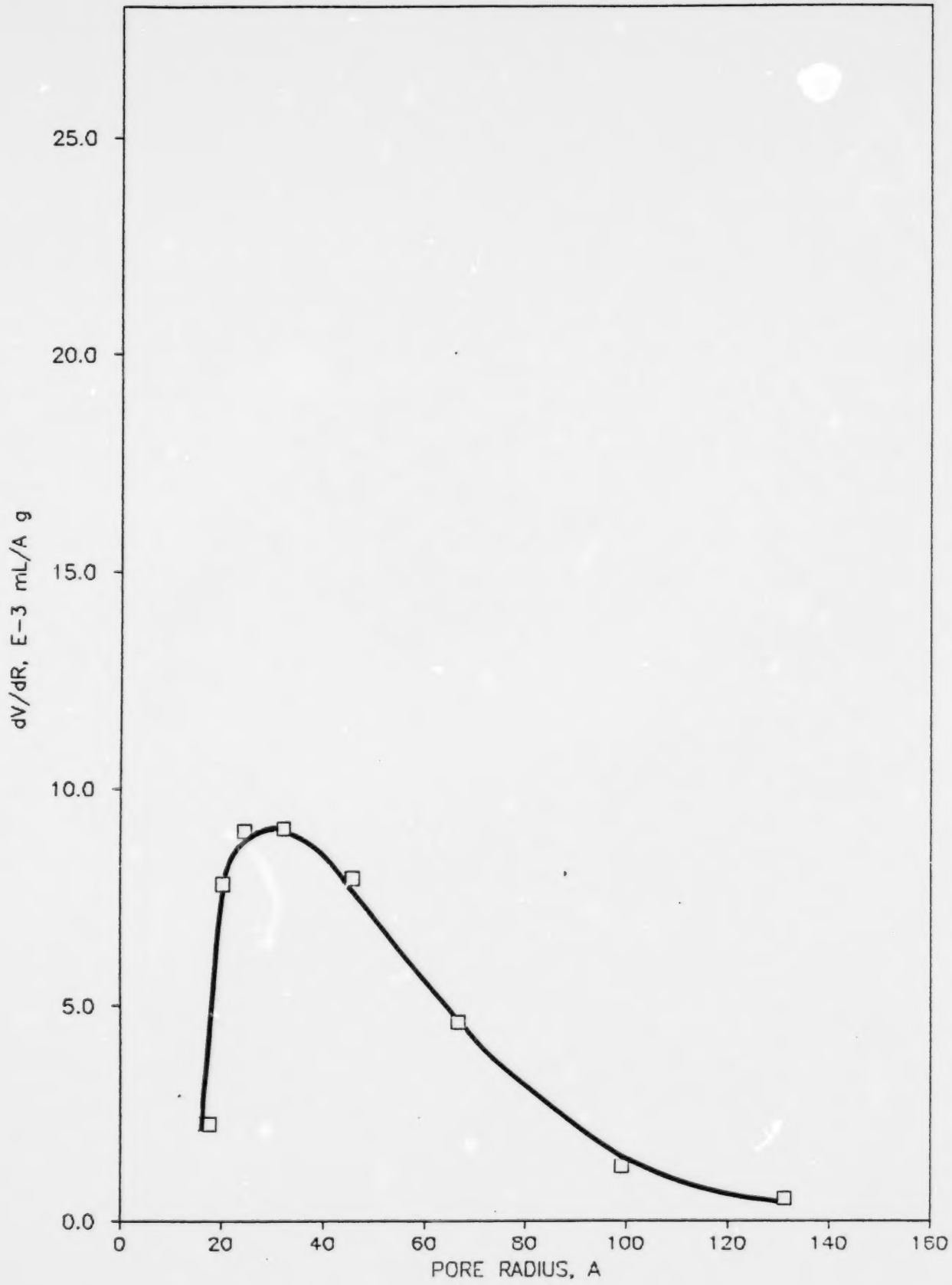

Fig. 3: Pore Volume Distribution of the Iron/Alumina Catalyst

PREPARATION OF IRON/SILICA CATALYST

1. Chemicals and Supports

(i) Iron Nitrate

For details, see item #1(i) under Preparation of Iron/Alumina Catalyst.

(ii) Silica

Formula: SiO_2

Supplier: Davison Specialty Chemical Co.
(W. R. Grace & Co.)
Curtis Bay Works
Baltimore, Maryland 21203

Description: (Provided by the Manufacturer)
Silica gel catalyst, Grade 57
Size: -3 +12 mesh
BET Area: 300 m^2/g
99.5% SiO_2

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: 288 ± 4 m^2/g
2. Pore Volume Distribution: See Fig. 4

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of silica was placed in a large stainless steel bowl and dried in a Blue M-Convection oven at 150°C for 24 h. We used two bowls: one contained 1016 g of silica (Batch A) and the second contained 902.9 g (Batch B).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Fe on silica support, 387.2 g of iron nitrate was dissolved in 1189 mL of distilled water, and the resulting solution was slowly poured over the silica support with gentle and even mixing. This mixing continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation.

(b) Impregnation of Batch B: For this Batch, we dissolved 343.9 g of iron nitrate in 1056 mL of distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The catalyst was transferred from the bowls onto two flat pans (27 cm x 40 cm). These pans containing the catalyst were then covered with aluminum foil with holes in it (for the moisture to escape). The catalyst was dried in the Blue M-Convection oven for 24 h at 90°C.

(iv) Calcination of the Catalyst

The dried catalyst was transferred from the flat iron pans to porcelain bowls for the calcination step. The bowls were covered with stainless steel sheets with holes. These bowls were now placed in the oven. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

Batches A and B were well mixed by putting them together in a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the mixture for wt % Fe. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 5.

(vi) Sizing of the Catalyst

(a) Silica does not pelletize well. Therefore, the catalyst granules were gently milled and the required amount (600 g) of -6 +8 mesh sample was collected.

(b) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required amount (600 g) of the -70 +100 mesh catalyst.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The value obtained is presented in Fig. 5.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the above Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Fig. 6.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 5.

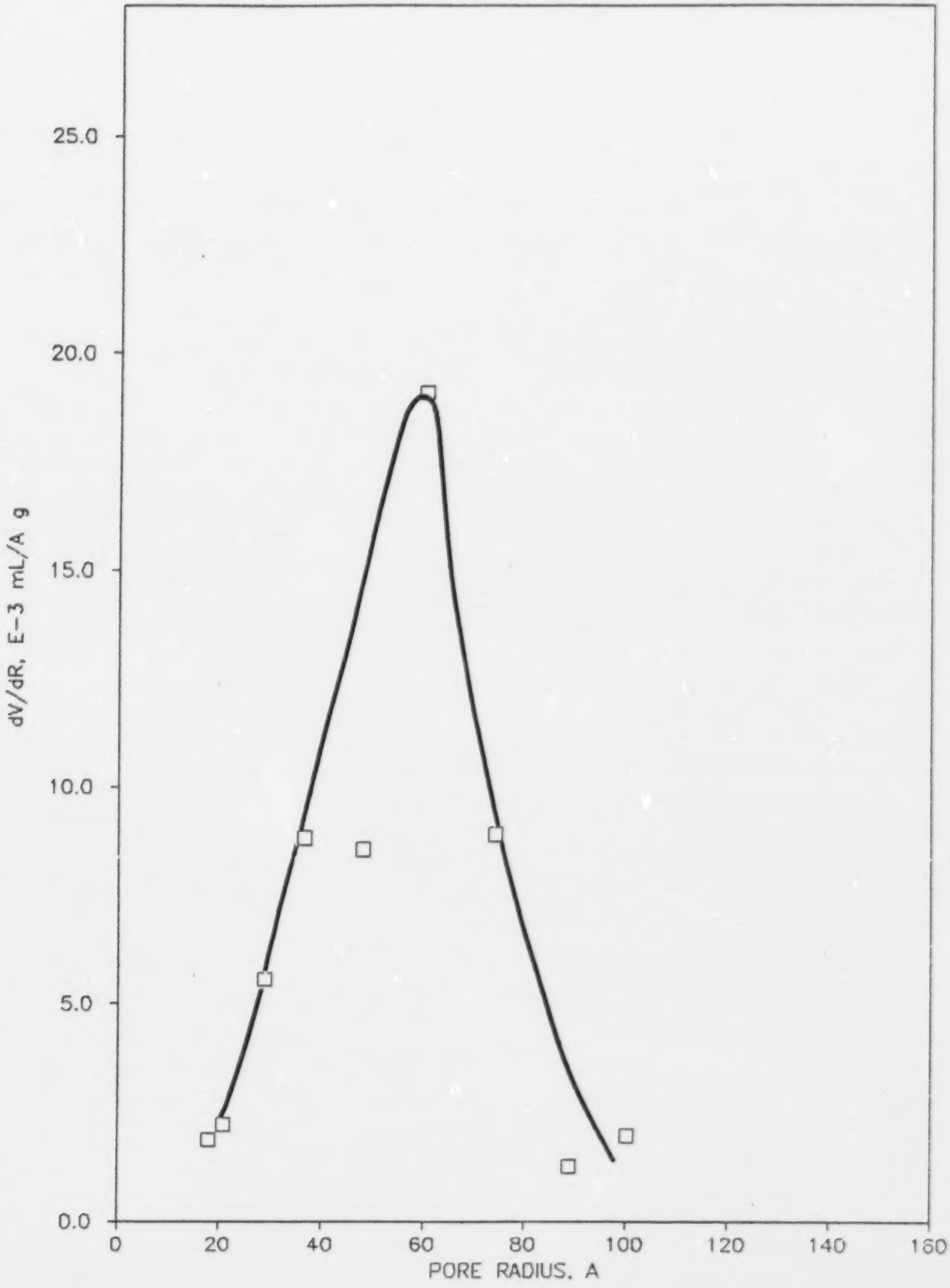

Fig. 4: Pore Volume Distribution of the Silica Support

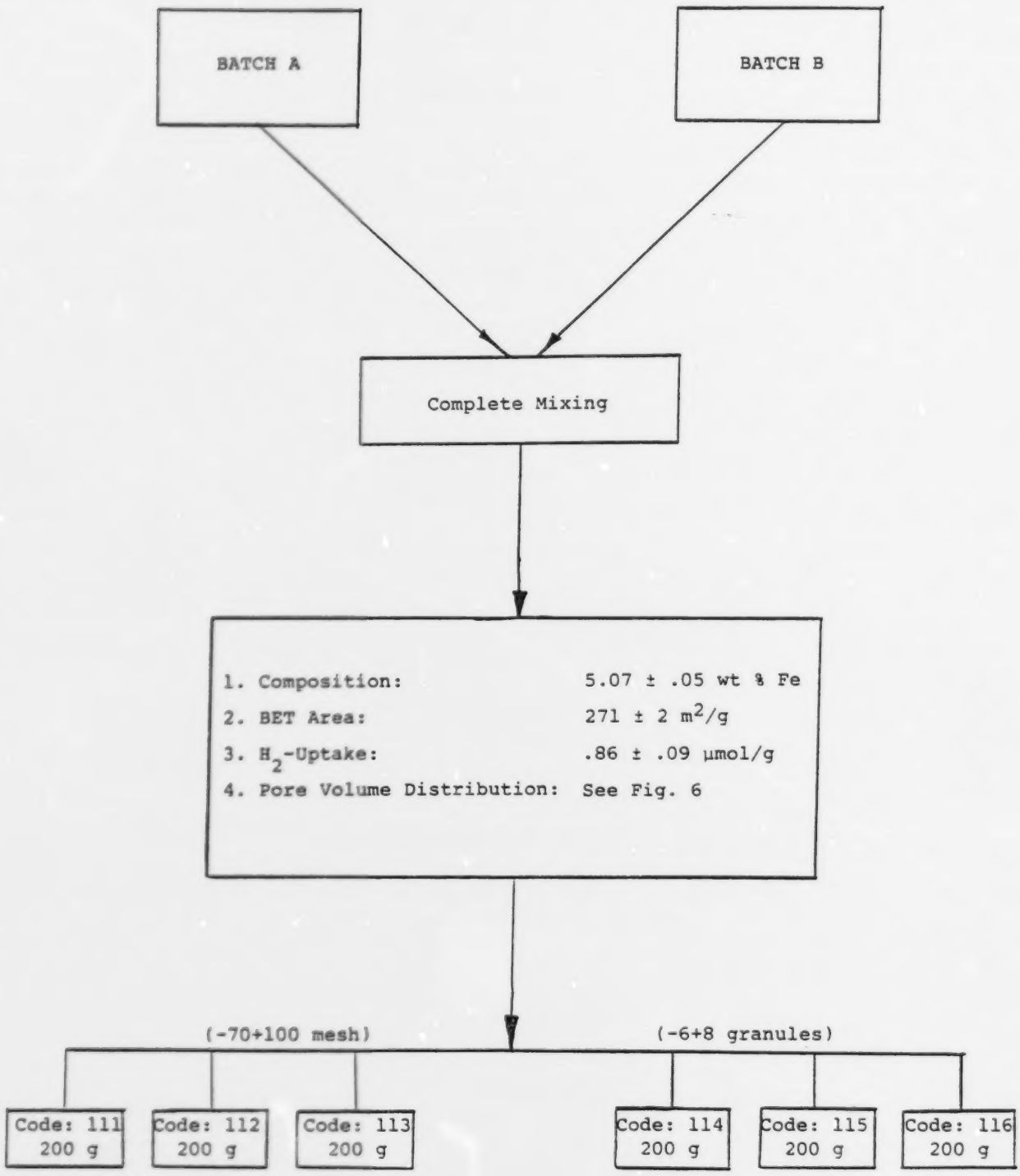
BATCH A
BATCH B
Complete Mixing
1. Composition: 5.07 ± .05 wt % Fe
2. BET Area: 271 ± 2 m²/g
3. H₂-Uptake: .86 ± .09 µmol/g
4. Pore Volume Distribution: See Fig. 6
(-70+100 mesh)
(-6+8 granules)
Code: 111 200 g
Code: 112 200 g
Code: 113 200 g
Code: 114 200 g
Code: 115 200 g
Code: 116 200 g

Fig. 5. Preparation and Characterization of the Iron/Silica Catalyst

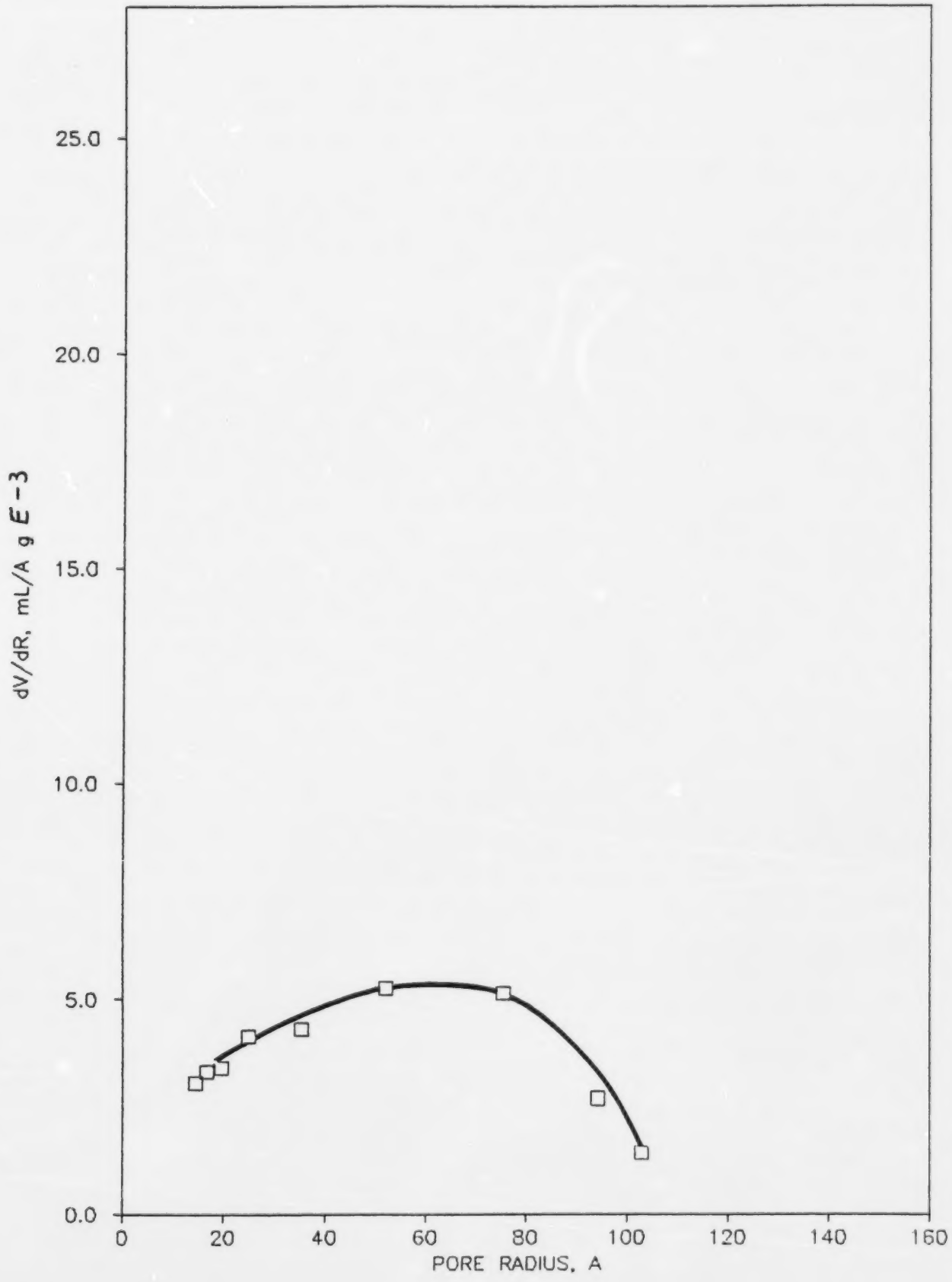

Fig. 6: Pore Volume Distribution of the Iron/Silica Catalyst

PREPARATION OF IRON/TITANIA CATALYST

1. Chemicals and Supports

(i) Iron Nitrate

For details, see item #1(i) under Preparation of Iron/Alumina Catalyst.

(ii) Titania

Formula: TiO_2

Supplier: Degussa Canada Ltd.
4261 Mainway Drive
Burlington, Ontario L7L 5N9

Description: (Provided by the Manufacturer)
P-25
Size: 30 microns
BET Area: 50 ± 15 m^2/g
Density: 150 g/L

Typical Analysis	wt %
TiO_2	99.5
SiO_2	.2
Al_2O_3	.3
FeO_2	.01

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: 55.7 ± 2.7m^2/g
2. Pore Volume Distribution: See Fig. 7

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of titania was placed in a large porcelain bowl and dried in a Blue M-Convection oven at 150°C for 24 h. We used two bowls: one contained 654.0 g (Batch A) and the second contained 902.4 g (Batch B).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Fe on titania support, 249.1 g of iron nitrate was dissolved in 817.5 mL of distilled water, and the resulting solution was slowly poured

over the titania support with gentle and even mixing. This mixing continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation. Impregnation was done in the porcelain bowls.

(b) Impregnation of Batch B: For this Batch, we dissolved 343.6 g of iron nitrate in 1128 mL of distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The bowls containing the catalyst paste (resulting from the impregnation step (ii)) were placed in the Blue M-Convection oven to dry at 90°C for 24 h. Care was taken to spread around the catalyst paste in the bowl for ease in drying. Also, the bowls were covered with aluminum foil (with a number of holes for the moisture to escape) to ensure that no catalyst was lost by convection currents in the oven.

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowls for the calcination step. The bowls were covered with the same aluminum foil used for drying of the catalyst. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

Batches A and B were <u>each</u> mixed well separately by putting them in a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the batches for wt % Fe. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 8.

(vi) Sizing of the Catalyst

(a) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required -70 +100 mesh catalyst. 200 g were obtained from Batch A and 400 g were obtained from Batch B.

(b) Pelletizing

The catalyst left after the required -70 +100 mesh fraction was obtained was made into 3 mm pellets. The catalyst was mixed with enough stearic acid to give 1 wt % stearic acid in the mixture. Care was taken to ensure even mixing. The pellets were made in the same way as described in iron/alumina catalyst pelletizing.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The values obtained were presented in Fig. 8.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Figs. 9 and 10.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-Uptake value. The value obtained is given in Fig. 8.

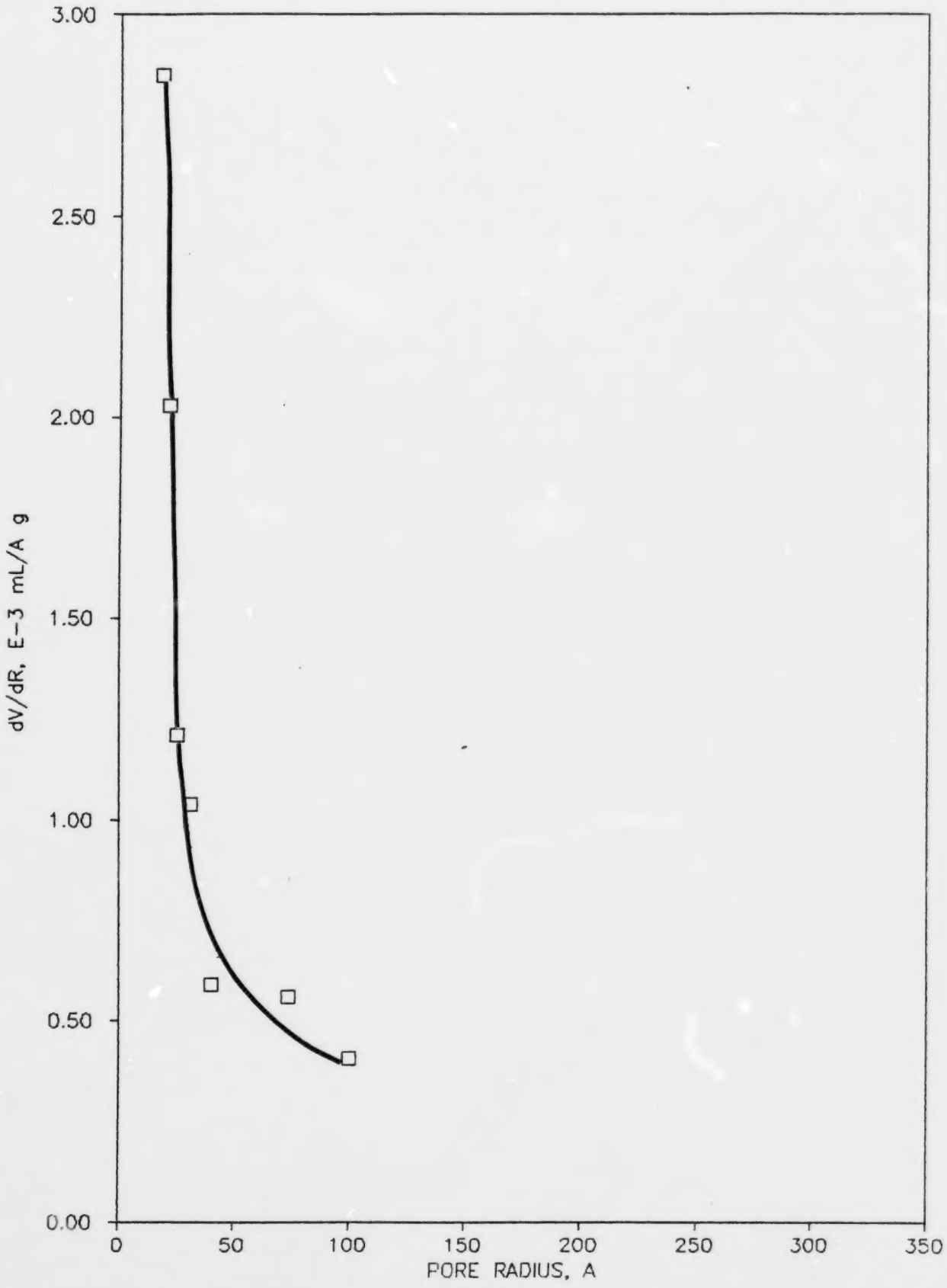

Fig. 7: Pore Volume Distribution of the Titania Support

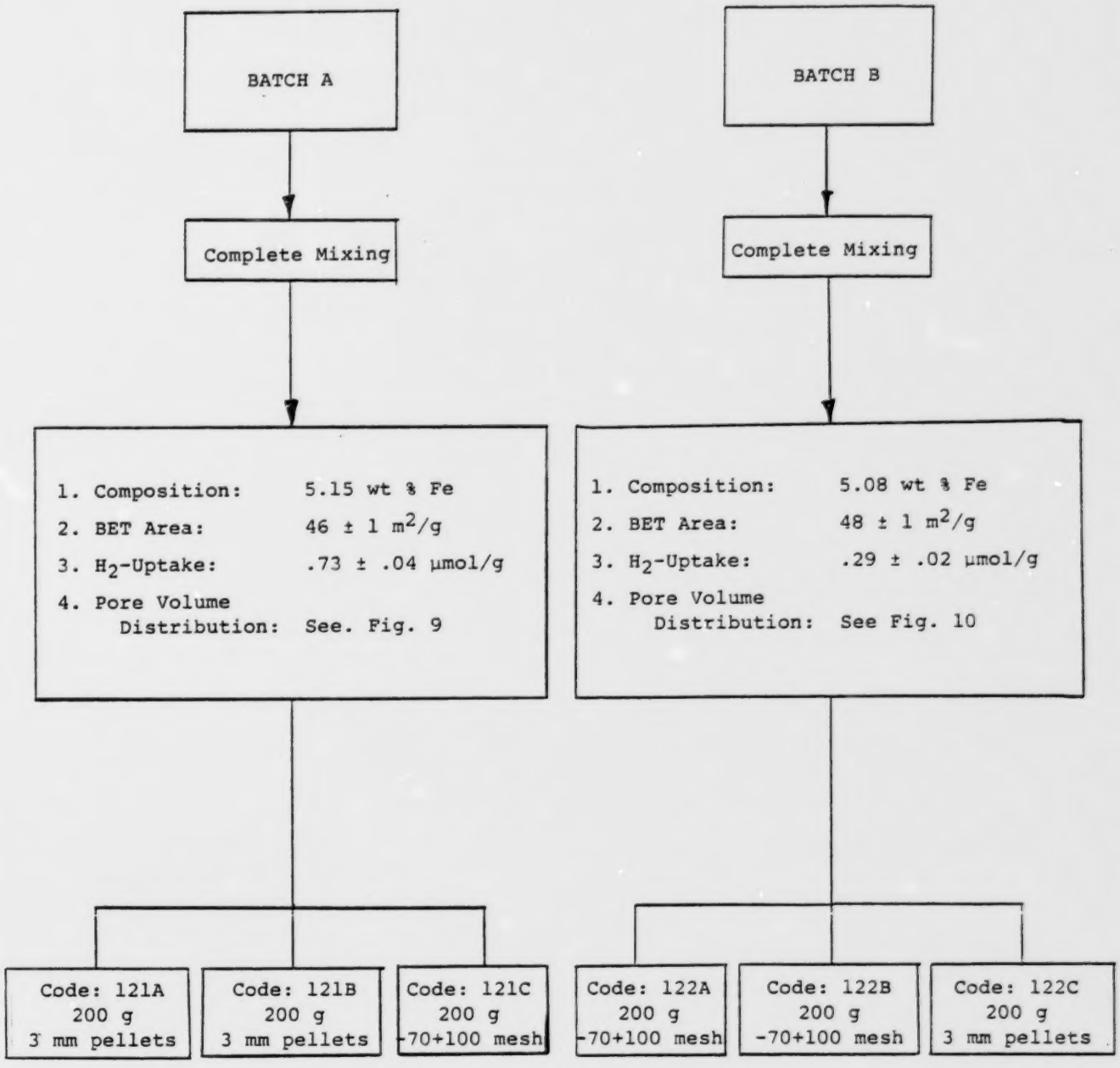
BATCH A
BATCH B
Complete Mixing
Complete Mixing
1. Composition: 5.15 wt % Fe
2. BET Area: 46 ± 1 m²/g
3. H₂-Uptake: .73 ± .04 µmol/g
4. Pore Volume Distribution: See. Fig. 9
1. Composition: 5.08 wt % Fe
2. BET Area: 48 ± 1 m²/g
3. H₂-Uptake: .29 ± .02 µmol/g
4. Pore Volume Distribution: See Fig. 10
Code: 121A 200 g 3 mm pellets
Code: 121B 200 g 3 mm pellets
Code: 121C 200 g -70+100 mesh
Code: 122A 200 g -70+100 mesh
Code: 122B 200 g -70+100 mesh
Code: 122C 200 g 3 mm pellets

Fig. 8. Preparation and Characterization of the Iron/Titania Catalyst

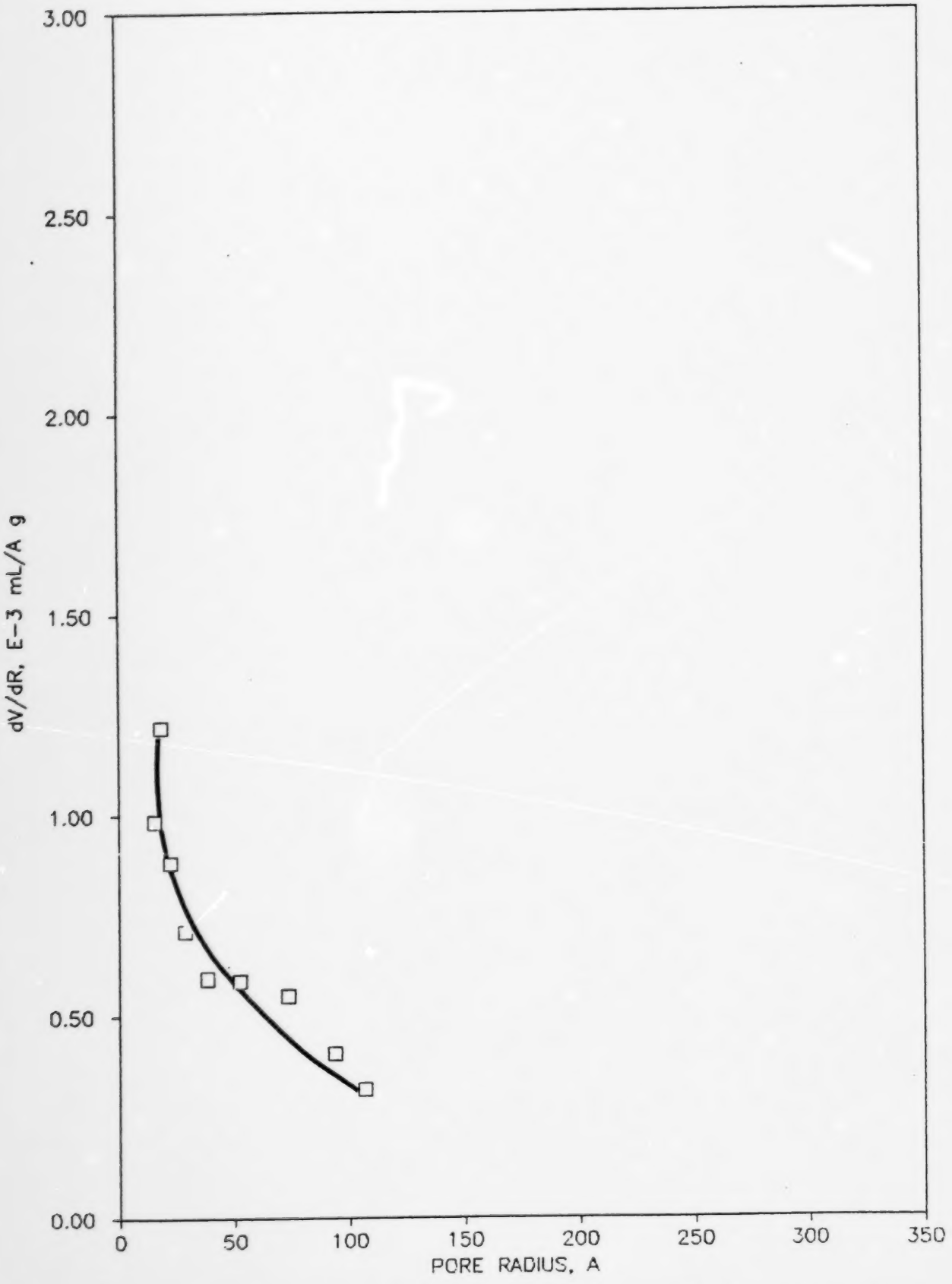

Fig. 9: Pore Volume Distribution of the Iron/Titania Catalyst (Batch A)

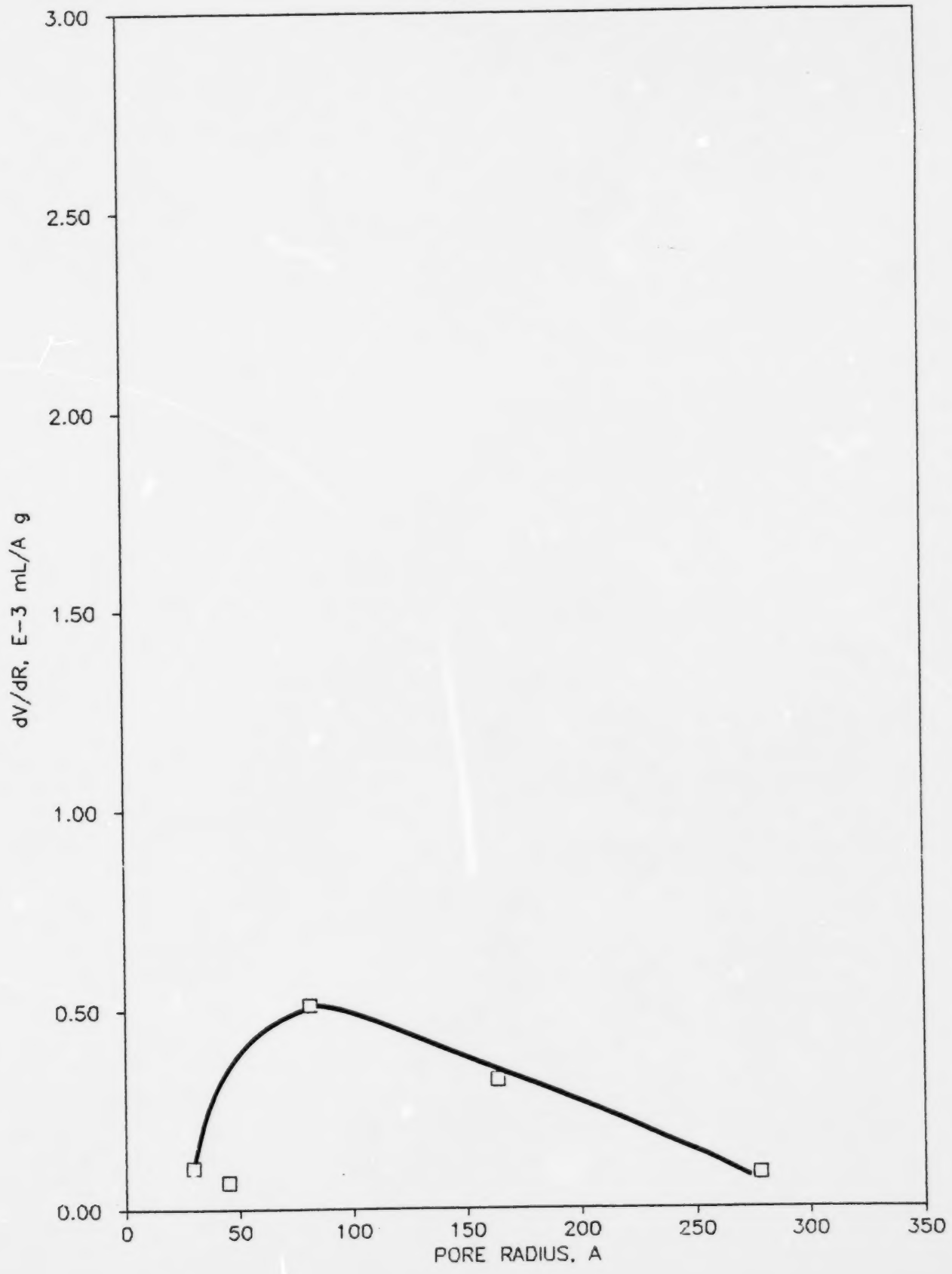

Fig. 10: Pore Volume Distribution of the Iron/Titania Catalyst (Batch B)

PREPARATION OF IRON/ZIRCONIA CATALYST

1. Chemicals and Supports

(i) Iron Nitrate

For details, see item #1(i) under Preparation of Iron/Alumina Catalyst.

(ii) Zirconia

Formula: ZrO_2

Supplier: Alfa Division, Ventron Corp.
152 Andover St.
Danvers, MA. 01923

Description: (provided by the Manufacturer)
99+% pure

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: $5.2 m^2/g$
2. Pore Volume Distribution: See Fig. 11

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of zirconia was placed in a large porcelain bowl and dried in a Blue M-Convection oven at 150°C for 24 h. The bowl contained 1524.6 g of zirconia.

(ii) Impregnation

In order to obtain 5 wt% Fe on zirconia support, 580.5g of iron nitrate was placed in a glass beaker and the beaker placed in the blue M-Convection oven at 100°C. The iron nitrate melted, resulting in a homogeneous solution. The solution was slowly poured over the zirconia support with gentle and even mixing. This mixing continued for 5 min. This time duration was found to be quite sufficient for complete impregnation. Mixing time was shorter than with other supports on account of the small volume of the zirconia. Also, after approximately 10 min the mixture starts to harden. Impregnation was carried out in a porcelain bowl.

(iii) Drying of the Catalyst

The bowl containing the catalyst was covered with aluminum foil (with a number of holes) and then put in the fume hood to dry for

16 h. After that the bowl was placed in the Blue M-Convection oven for 2 h at 90°C for further drying (the catalyst mass softens and was stirred intermittently at 1/2 h intervals to dry evenly). The resulting catalyst mass was agina placed in the fume hood to dry at the ambient temperature for 24 h. We adopted this procedure after a number of trials. The drying procedure had to be modified as it was found that a part of the catalyst mass becomes purple colored (vis-a-vis a normal pale brownish color) if drying took place at 90°C.

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowl for the calcination step. The bowl was covered with the aluminum foil. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

The catalyst was mixed well by putting it into a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed for wt % Fe. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 12.

(vi) Sizing of the Catalyst

(a) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required 600 g of -70 +100 mesh catalyst.

(b) Pelletizing

(i) Problems in Pelletizing

With 1 wt% stearic acid good pellets could not be formed. Additional experimentation showed that 5 wt% stearic acid gives reasonably good pellets. It was also very difficult to fill the 3mm dies will enough powder in order to obtain a strong grid sized pellet. In the unsuccessful attempts to make good, strong 3mm pellets all our dies either bent or broke. After discussion with the Scientific Authority it was decided to make 5mm pellets containing 5 wt% stearic acid. These pellets were tested in a 35 cm high column for mechanical strength. After three days there was no breakage of any pellets. Hence, 600g of pellets were made in 5 x 5 mm size.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The values obtained are presented in Fig. 12.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Fig. 13.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 12.

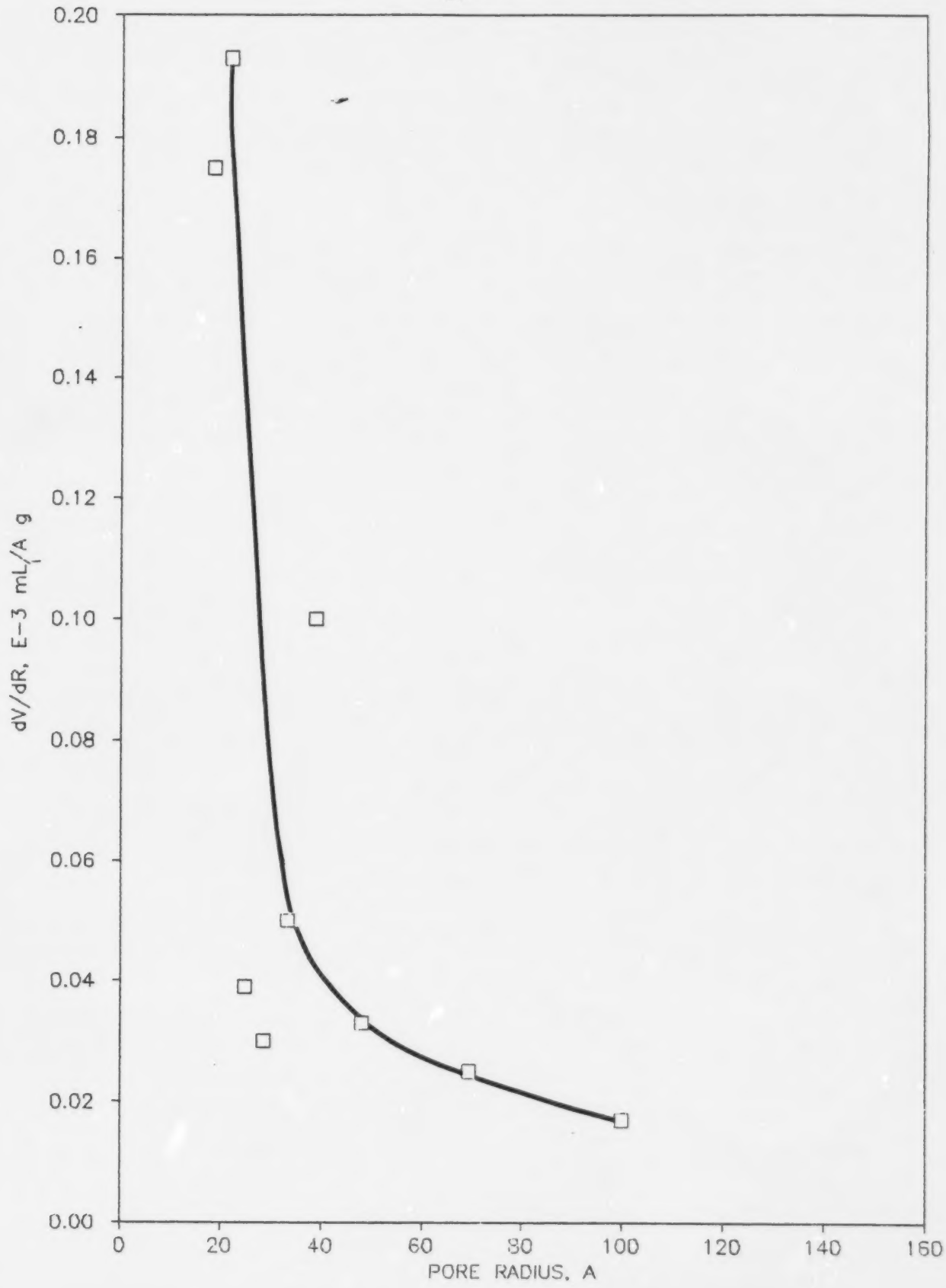

Fig. 11: Pore Volume Distribution of the Zirconia Support

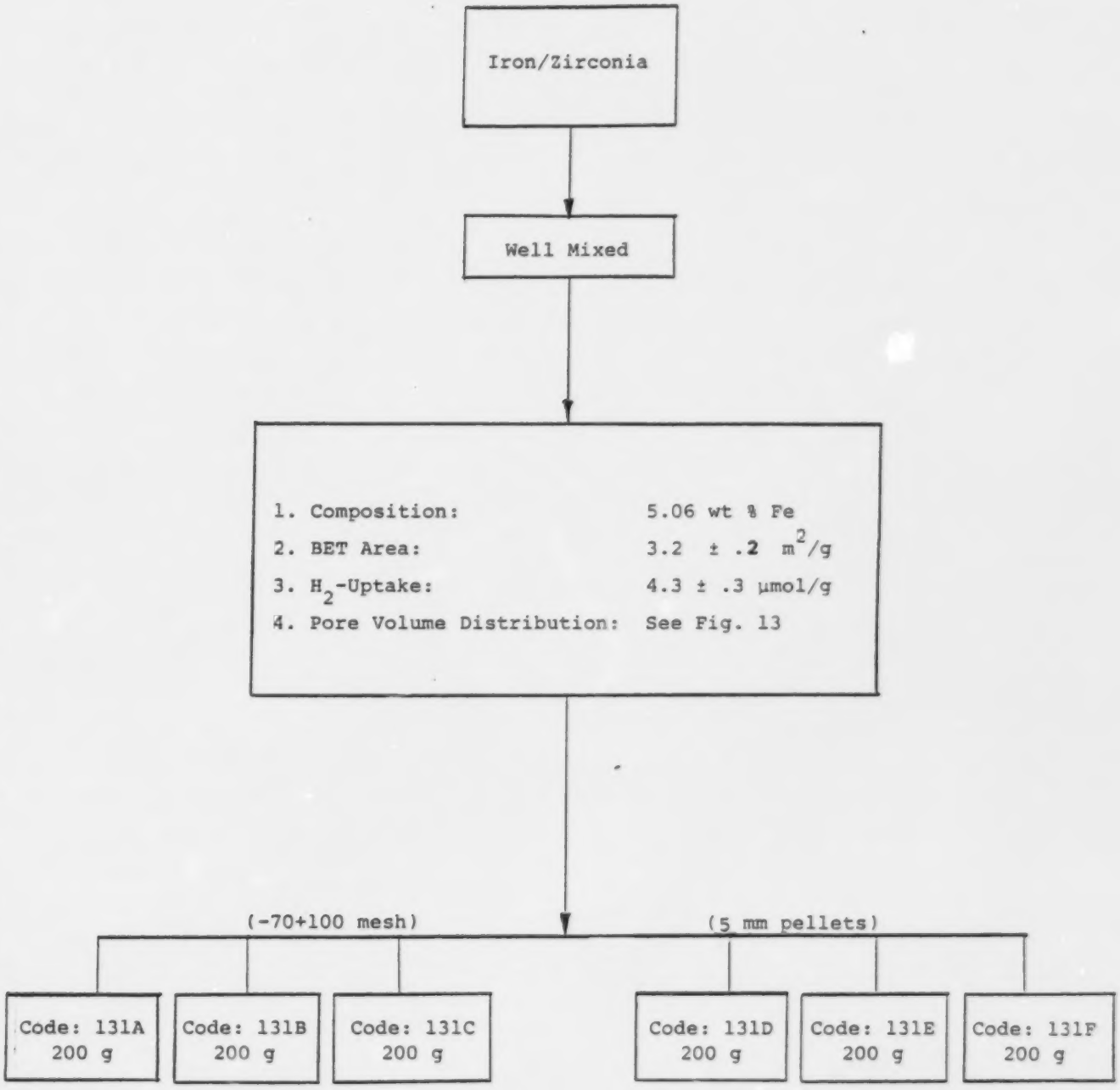
Iron/Zirconia
Well Mixed
1. Composition: 5.06 wt % Fe
2. BET Area: 3.2 ± .2 m²/g
3. H₂-Uptake: 4.3 ± .3 µmol/g
4. Pore Volume Distribution: See Fig. 13
(-70+100 mesh)
(5 mm pellets)
Code: 131A 200 g
Code: 131B 200 g
Code: 131C 200 g
Code: 131D 200 g
Code: 131E 200 g
Code: 131F 200 g

Fig. 12. Preparation and Characterization of the Iron/Zirconia Catalyst

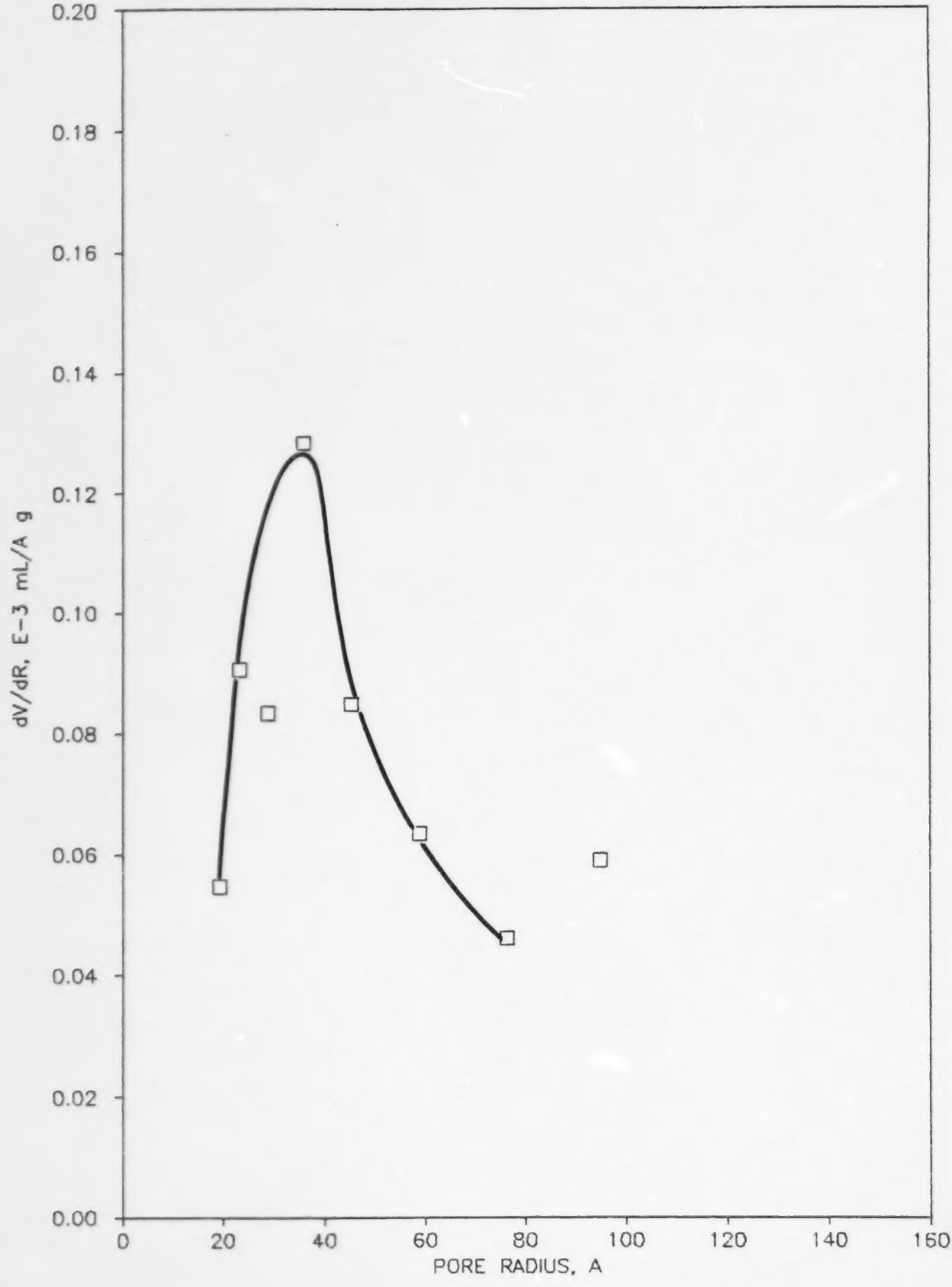

Fig. 13: Pore Volume Distribution of the Iron/Zirconia Catalyst

PREPARATION OF NICKEL/ALUMINA CATALYST

1. Chemicals and Supports

(i) Nickel Nitrate

Formula: $Ni(NO_3)_2 \cdot 6\ H_2O$

Supplier: Alfa Products
Thiokol/Ventron Div.
Danvers, Mass. 01923

Description: Puratronic
Purity - 90.9985 wt % (Metal Basis)

Alumina	
Bismuth	
Calcium	
Copper	each less then 1 ppm
Iron	
Magnesium	
Molybdenum	
Silicon	

(ii) Alumina

For details, see item #1(ii) under Preparation of Iron/Alumina Catalyst.

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristic of the Support: The following were measured in our laboratory.

1. BET Area: $278 \pm 2\ m^2/g$
2. Pore Volume Distribution: See Fig. 1

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of alumina was placed in a large porcelain bowl and dried in a Blue M-Convection oven at 150°C for 24 h. We used three bowls: one contained 705.1 g (Batch A), the second contained 944.6 (Batch B), and the third contained 284.9 g (Batch C).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Ni on silica support, 186.0 g of nickel nitrate was dissolved in 846.1 mL of distilled water, and the resulting solution was slowly poured over the alumina support with gentle and even mixing. This

mixing continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation. Impregnation took place in the porcelain bowls.

(b) Impregnation of Batch B: For this Batch, we dissolved 251.6 g of nickel nitrate in 1133.5 mL of distilled water in order to carry out the impregnation.

(c) Impregnation of Batch C: For this Batch, we dissovled 75.1 g of nickel nitrate in 341 mL of distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The bowls containing the catalyst paste (resulting from the impregnation step (ii)) were placed in the Blue M-Convection oven to dry at 90°C for 24 h. The bowls were stirred once every half hour for the first 1 1/2 hours. Also, the bowls were covered with aluminum foil (with a number of holes for the moisture to escape) to ensure that no catalyst was lost by convection currents in the oven.

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowls for the calcination step. The bowls were covered with the same aluminum foil used for drying of the catalyst. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

Batches A, B and C were each mixed well separately by putting them in a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the batches for wt % Ni. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 14.

(vi) Sizing of the Catalyst

(a) -70 +100 Mesh Powder

After calcination, the catalyst was a powder of particle size smaller than 100 mesh. 1 1/8" diameter pellets of 7-8 grams each were made. 3000 psi pressure was applied for one minute to make the pellets. The pellets were crushed and sieved to obtain the required amount (600 g) of -70 +100 mesh powder.

(b) Pelletizing

The catalyst was mixed with enough stearic acid to give 1 wt % stearic acid in the mixture. Care was taken to ensure even mixing. The 3 mm pellets were made in the same way as described in 'iron/alumina catalyst pelletizing'.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface Areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The values obtained are presented in Fig. 14.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Figs. 15, 16, and 16A.

(c) H_2-Uptake

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 14.

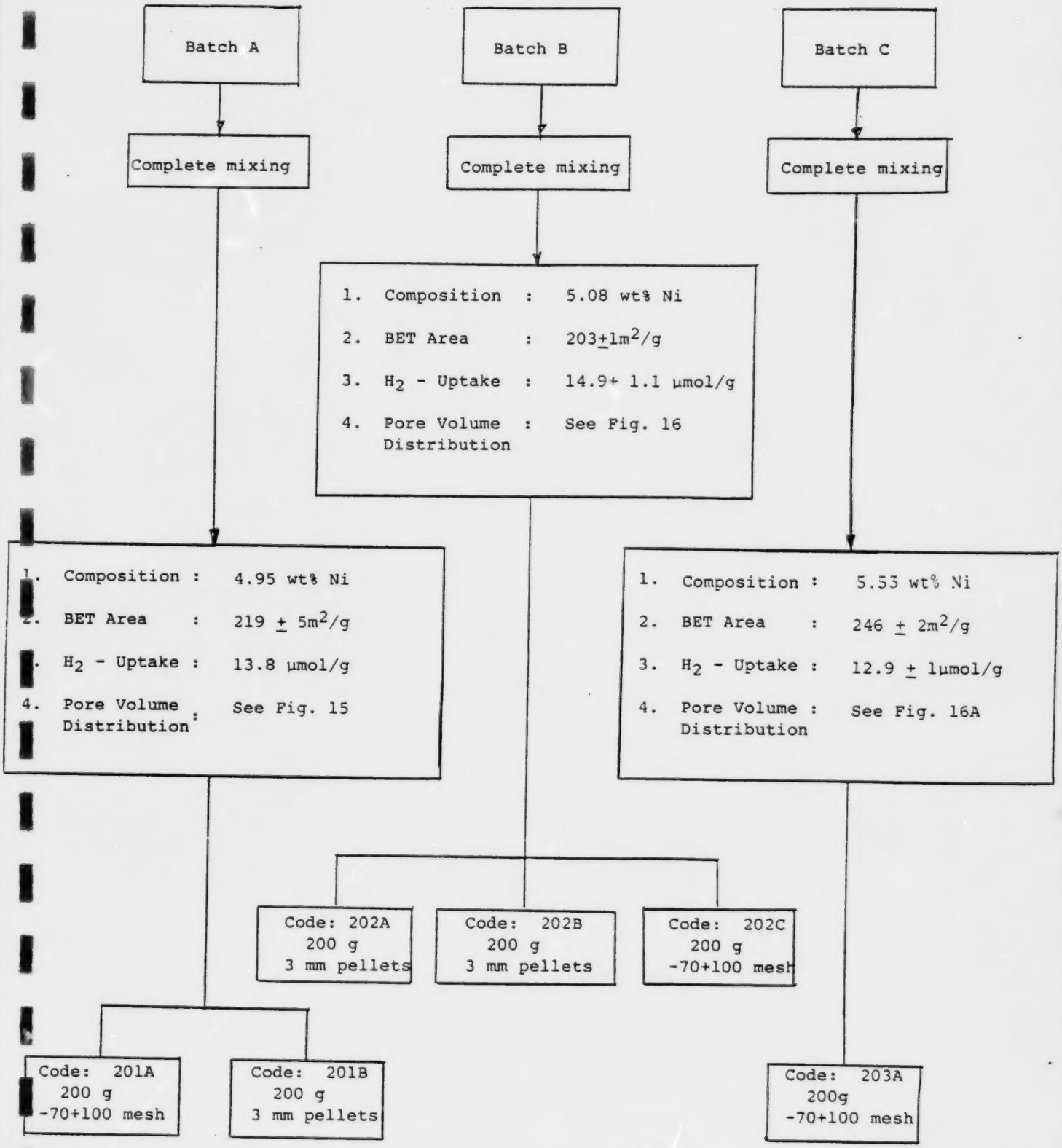
Batch A
Batch B
Batch C
Complete mixing
Complete mixing
Complete mixing
1. Composition : 5.08 wt% Ni
2. BET Area : 203±1m²/g
3. H2 - Uptake : 14.9± 1.1 µmol/g
4. Pore Volume Distribution : See Fig. 16
1. Composition : 4.95 wt% Ni
2. BET Area : 219 ± 5m²/g
3. H2 - Uptake : 13.8 µmol/g
4. Pore Volume Distribution : See Fig. 15
1. Composition : 5.53 wt% Ni
2. BET Area : 246 ± 2m²/g
3. H2 - Uptake : 12.9 ± 1µmol/g
4. Pore Volume Distribution : See Fig. 16A
Code: 202A 200 g 3 mm pellets
Code: 202B 200 g 3 mm pellets
Code: 202C 200 g -70+100 mesh
Code: 201A 200 g -70+100 mesh
Code: 201B 200 g 3 mm pellets
Code: 203A 200g -70+100 mesh

Fig. 14: Preparation and Characterization of the Nickel/Alumina Catalyst

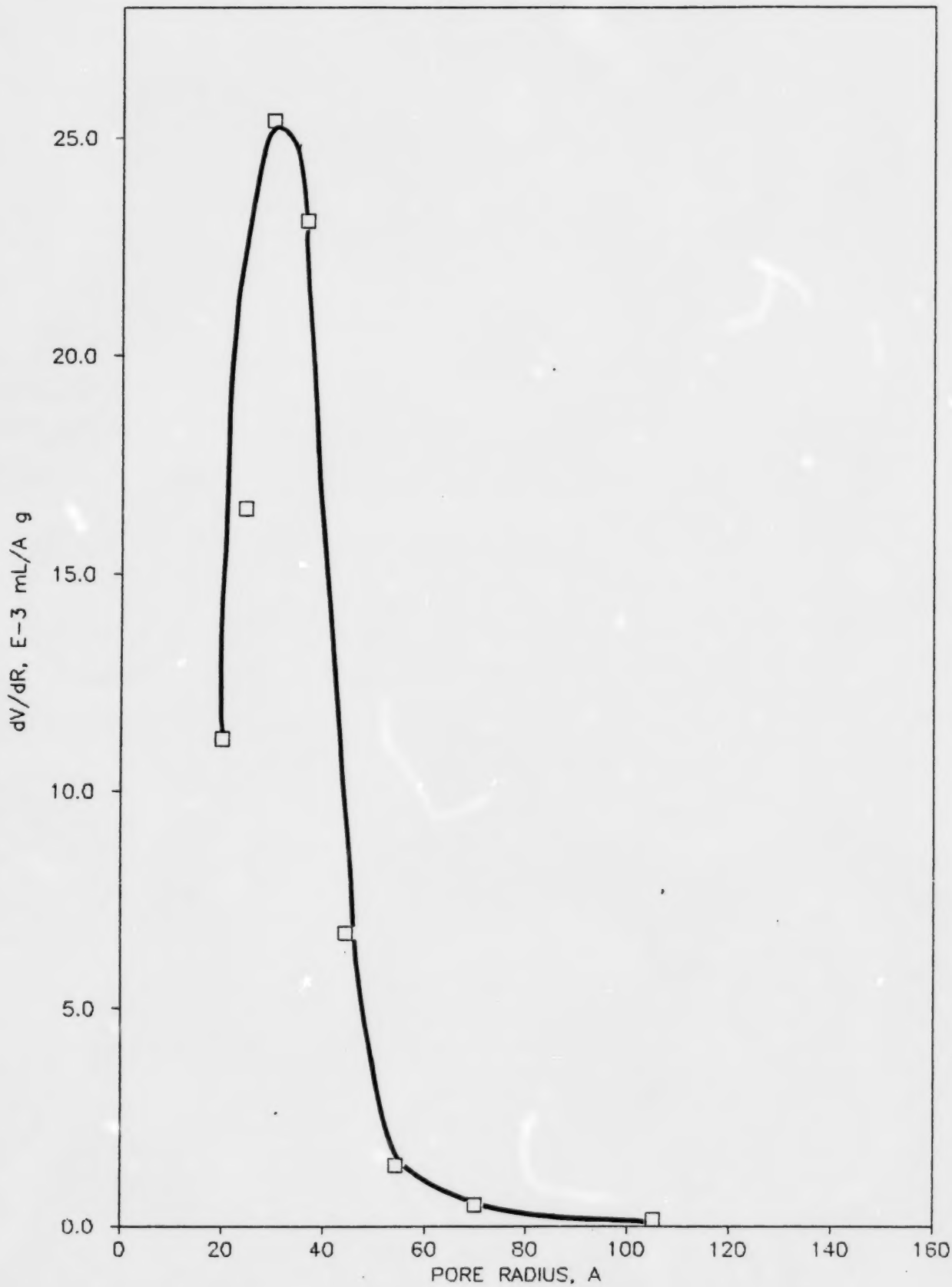

Fig. 15: Pore Volume Distribution of the Nickel/Alumina Catalyst (Batch A)

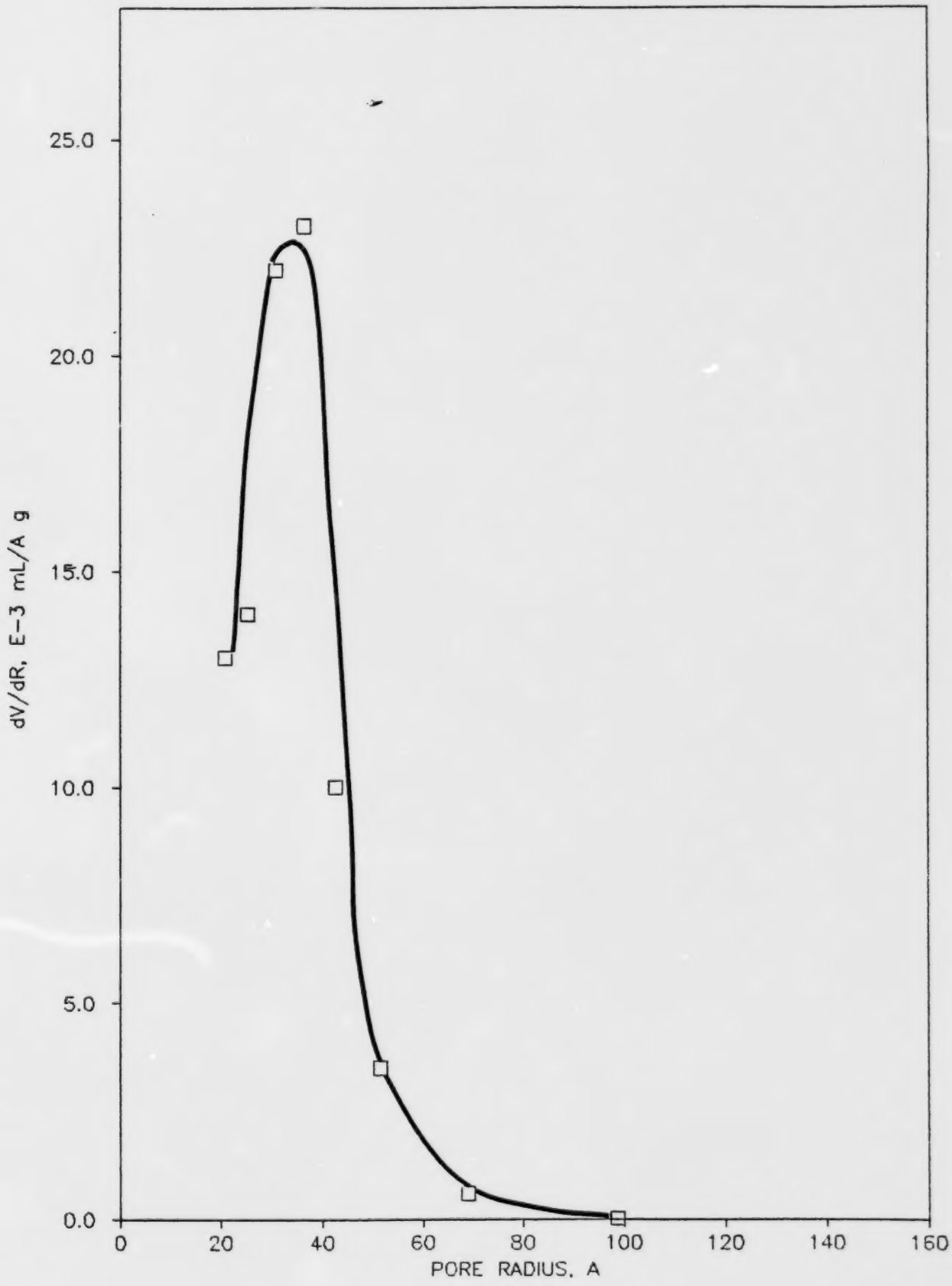

Fig. 16: Pore Volume Distribution of the Nickel/Alumina Catalyst (Batch B)

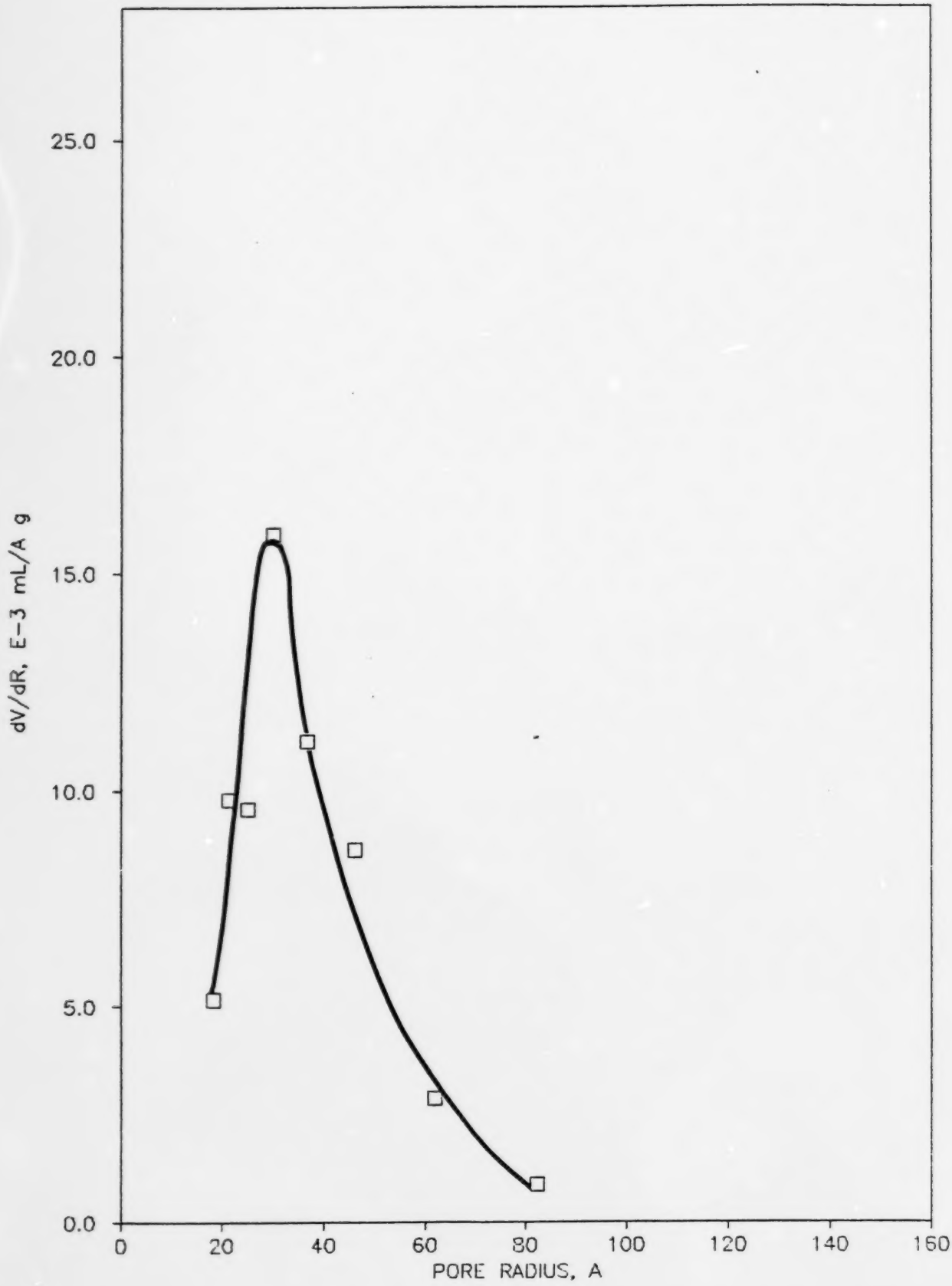

Fig. 16A: Pore Volume Distribution of the Nickel/Alumina Catalyst (Batch C)

PREPARATION OF NICKEL/SILICA CATALYST

1. Chemicals and Supports

(i) Nickel Nitrate

For details, see item #1(i) under Preparation of Nickel/Alumina Catalyst.

(ii) Silica

For details, see item #1(ii) under Preparation of Iron/Silica Catalyst.

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: 288 ± 4 m^2/g
2. Pore Volume Distribution: See Fig. 4

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of silica was placed in a large porcelain bowl and dried in a Blue-M-Convection oven at 150°C for 24 h. We used two bowls: one contained 826.9 g (Batch A) and the second contained 824.0 g (Batch B).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Ni on silica support, 215.8 g of nickel nitrate was dissolved in 976 mL of distilled water, and the resulting solution was slowly poured over the silica support with gentle and even mixing. This mixing continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation. Impregnation took place in the porcelain bowls.

(b) Impregnation of Batch B: For this Batch, we dissolved 214.9 g of nickel nitrate in 972 mL of distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The bowls containing the catalyst granules (resulting from the impregnation step (ii)) were placed in the Blue M-Convection oven to dry at 90°C for 24 h. The bowls were stirred once an hour for the first four hours. Also, the bowls were covered with aluminum foil (with a number of holes for the moisture to escape) to ensure t h a t no catalyst was lost by convection currents in the oven.

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowls for the calcination step. The bowls were covered with the same aluminum foil used for drying of the catalyst. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

Batches A and B were each mixed well separately by putting them in a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the batches for wt % Ni. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 17.

(vi) Sizing of the Catalyst

(a) Silica does not pelletize well. Therefore, the catalyst granules were gently milled and the required amount (600 g) of -6 +8 mesh sample was collected.

(b) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required amount (600 g) of the -70 +100 mesh catalyst.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The values obtained are presented in Fig. 17.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Figs. 18 and 19.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 17.

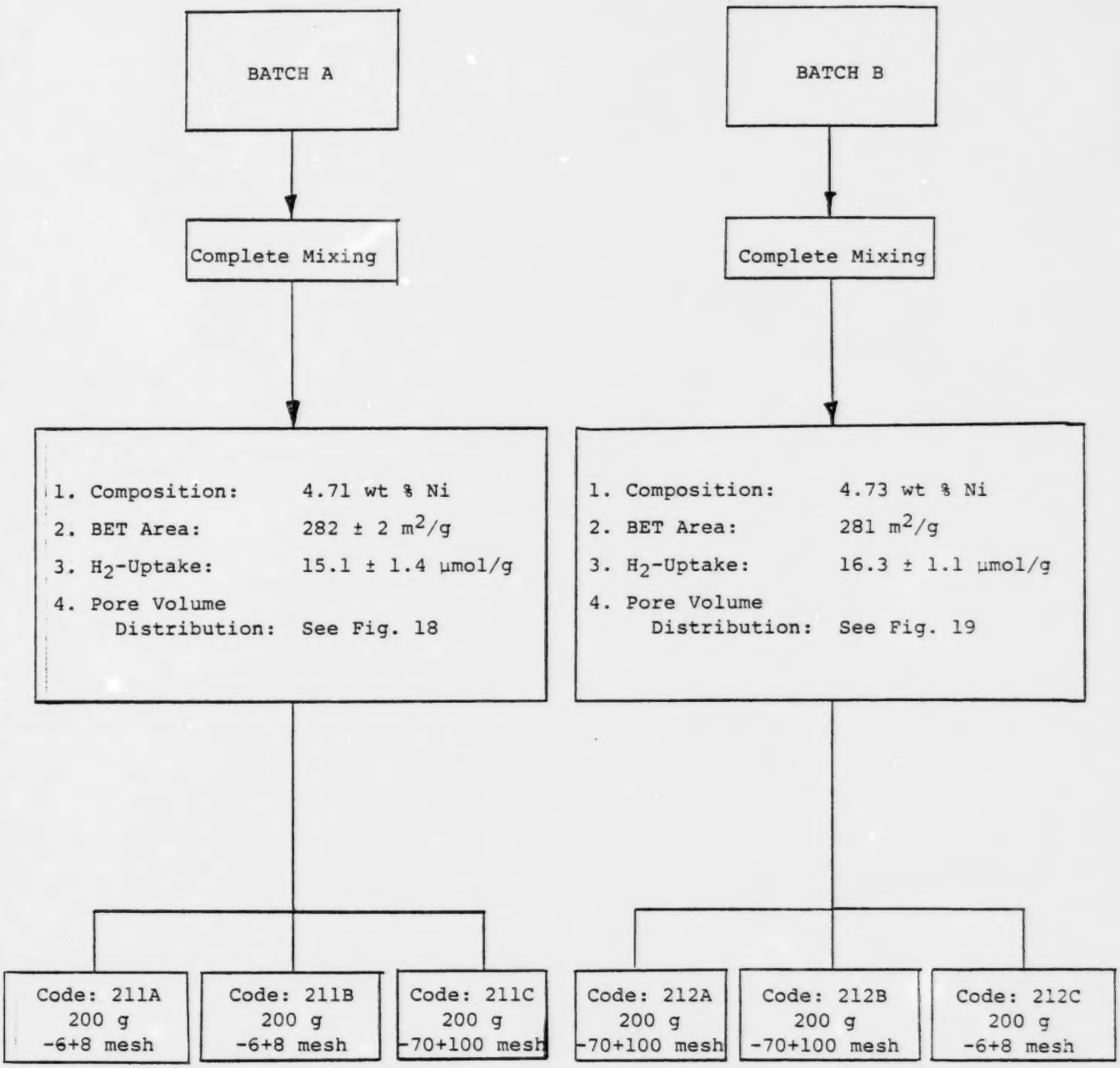
BATCH A
BATCH B
Complete Mixing
Complete Mixing
1. Composition: 4.71 wt % Ni
2. BET Area: 282 ± 2 m²/g
3. H₂-Uptake: 15.1 ± 1.4 µmol/g
4. Pore Volume Distribution: See Fig. 18
1. Composition: 4.73 wt % Ni
2. BET Area: 281 m²/g
3. H₂-Uptake: 16.3 ± 1.1 µmol/g
4. Pore Volume Distribution: See Fig. 19
Code: 211A 200 g -6+8 mesh
Code: 211B 200 g -6+8 mesh
Code: 211C 200 g -70+100 mesh
Code: 212A 200 g -70+100 mesh
Code: 212B 200 g -70+100 mesh
Code: 212C 200 g -6+8 mesh

Fig. 17. Preparation and Characterization of the Nickel/Silica Catalyst

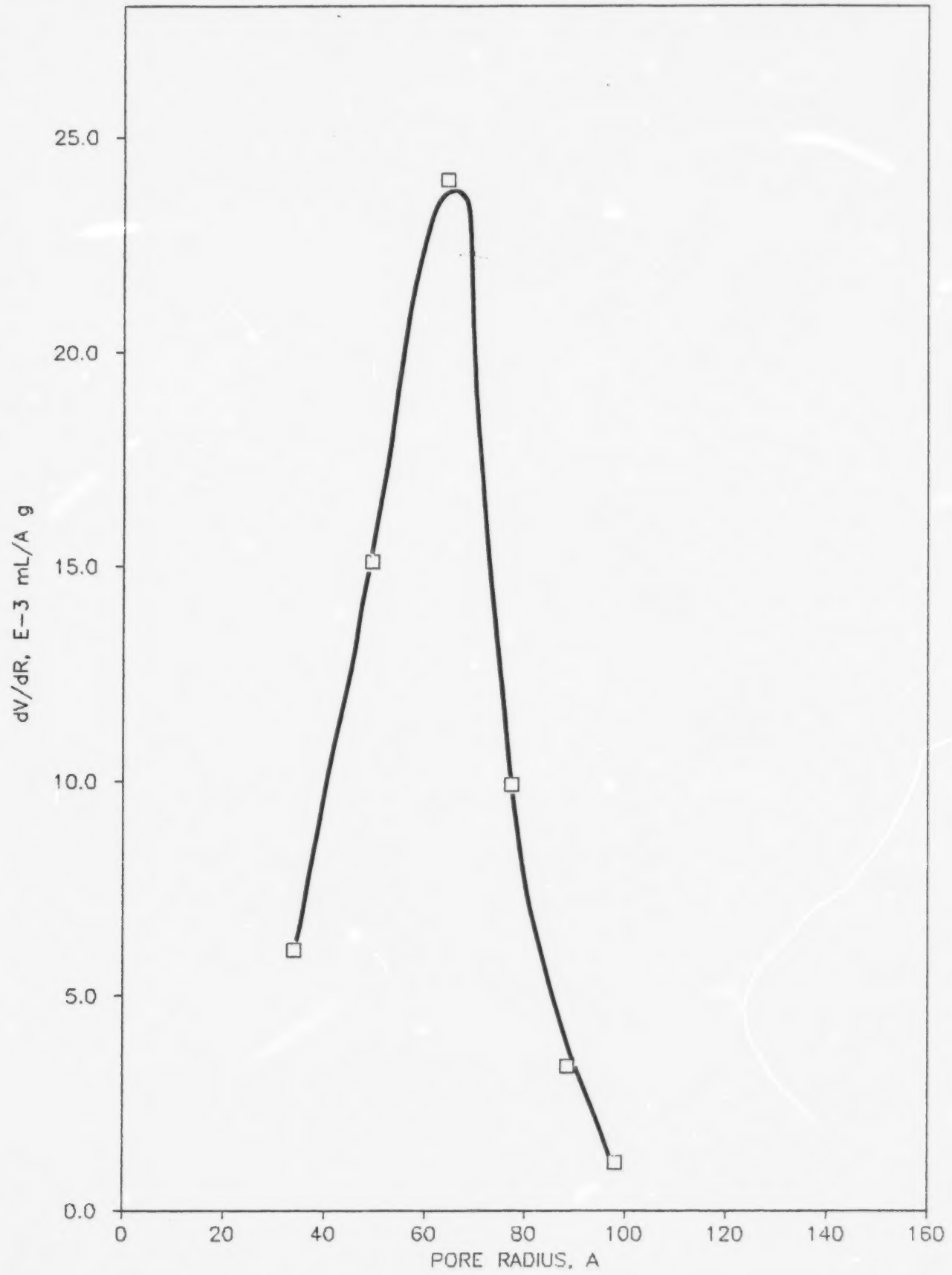

Fig. 18: Pore Volume Distribution of the Nickel/Silica Catalyst (Batch A)

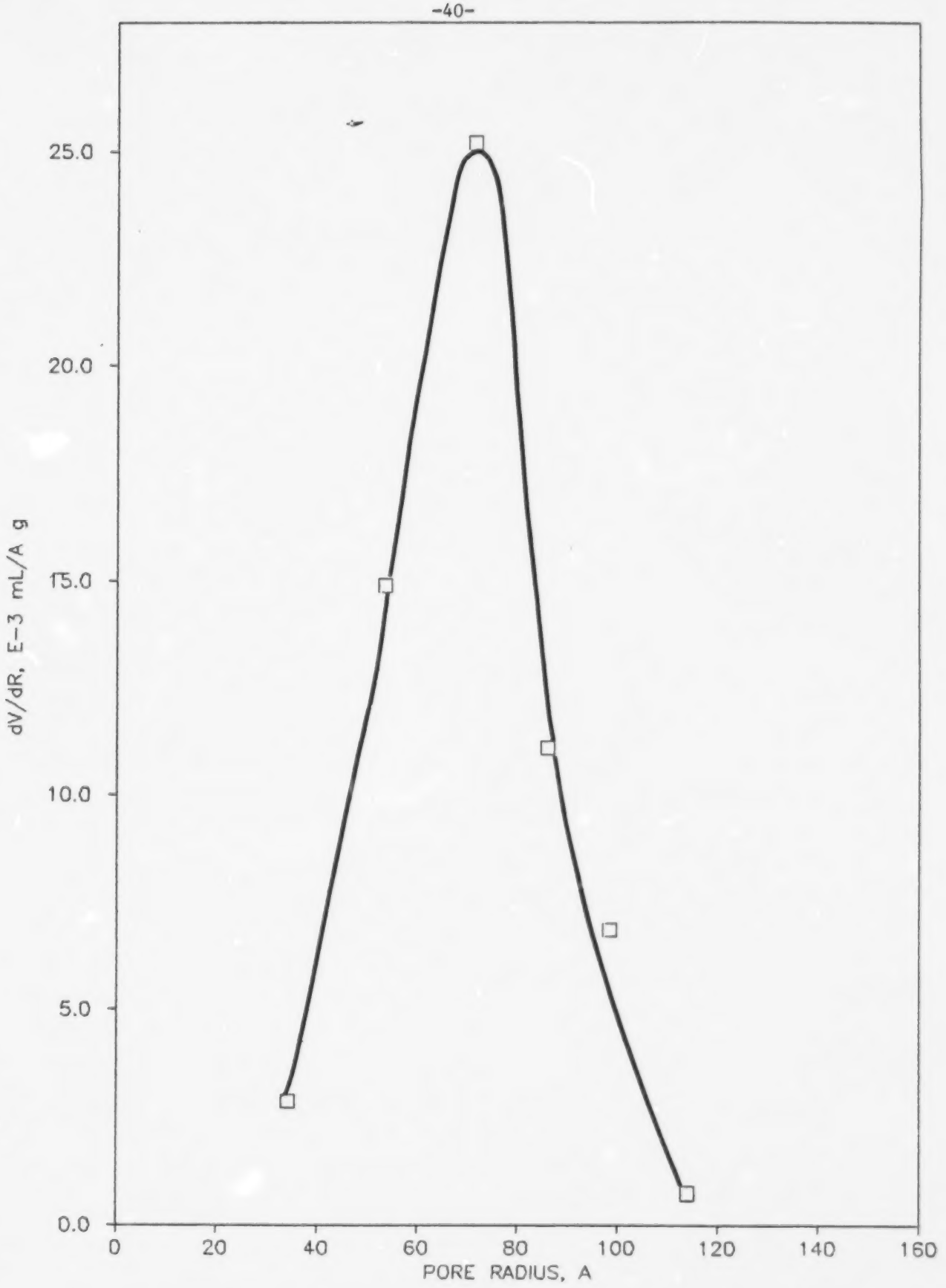

Fig. 19: Pore Volume Distribution of the Nickel/Silica Catalyst (Batch B)

PREPARATION OF NICKEL/TITANIA CATALYST

1. Chemicals and Supports

(i) Nickel Nitrate

For details, see item #1(i) under Preparation of Nickel/Alumina Catalyst.

(ii) Titania

For details, see item #1(ii) under Preparation of Iron/Titania Catalyst.

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: $58.7 \pm 2.7 m^2/g$
2. Pore Volume Distribution: See Fig. 7

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of titania was placed in a large porcelain bowl and dried in a Blue M-Convection oven at 150°C for 24 h. We used two bowls. One contained 1085.7 g (Batch A) and the second contained 585.3 g (Batch B).

(ii) Impregnation

(a) Impregnation of Batch A: In order to obtain 5 wt % Ni on titania support, 286.3 g of nickel nitrate in 1357 mL of distilled water and the resulting solution was dissolved slowly and poured over the titania support with gentle and even mixing. This mixing continued for 15 min. This time duration was found to be quite sufficient for complete impregnation. These numbers are based on our preliminary work to achieve incipient impregnation. Impregnation took place in the porcelain bowls.

(b) Impregnation of Batch B: For this Batch, we dissolved 154.3 g of nickel nitrate in 732 mL of distilled water in order to carry out the impregnation.

(iii) Drying of the Catalyst

The bowls containing the catalyst paste (resulting from the impregnation step (ii)) were placed in the Blue M-Convection oven to dry at 90°C for 24 h. Care was taken to spread around the catalyst paste in the bowl for ease in drying. Also, the bowls were covered

with aluminum foil (with a number of holes for the moisture to escape) to ensure that no catalyst was lost by convection currents in the oven.

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowls for the calcination step. The bowls were covered with the same aluminum foil used for drying of the catalyst. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

Batches A and B were each mixed well separately by putting them in a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the batches for wt % Ni. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 20.

(vi) Sizing of the Catalyst

(a) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required -70 +100 mesh catalyst. 400 g were obtained from Batch A, 200 g were obtained from Batch B.

(b) Pelletizing

The catalyst left after the required -70 +100 mesh fraction was obtained was made into 3 mm pellets. The catalyst was mixed with enough stearic acid to give 1 wt % stearic acid in the mixture. Care was taken to ensure even mixing. The pellets were made in the same way as described in 'iron/alumina catalyst pelletizing'.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surface areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The values obtained are presented in Fig. 20.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Figs. 21 and 22.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 20.

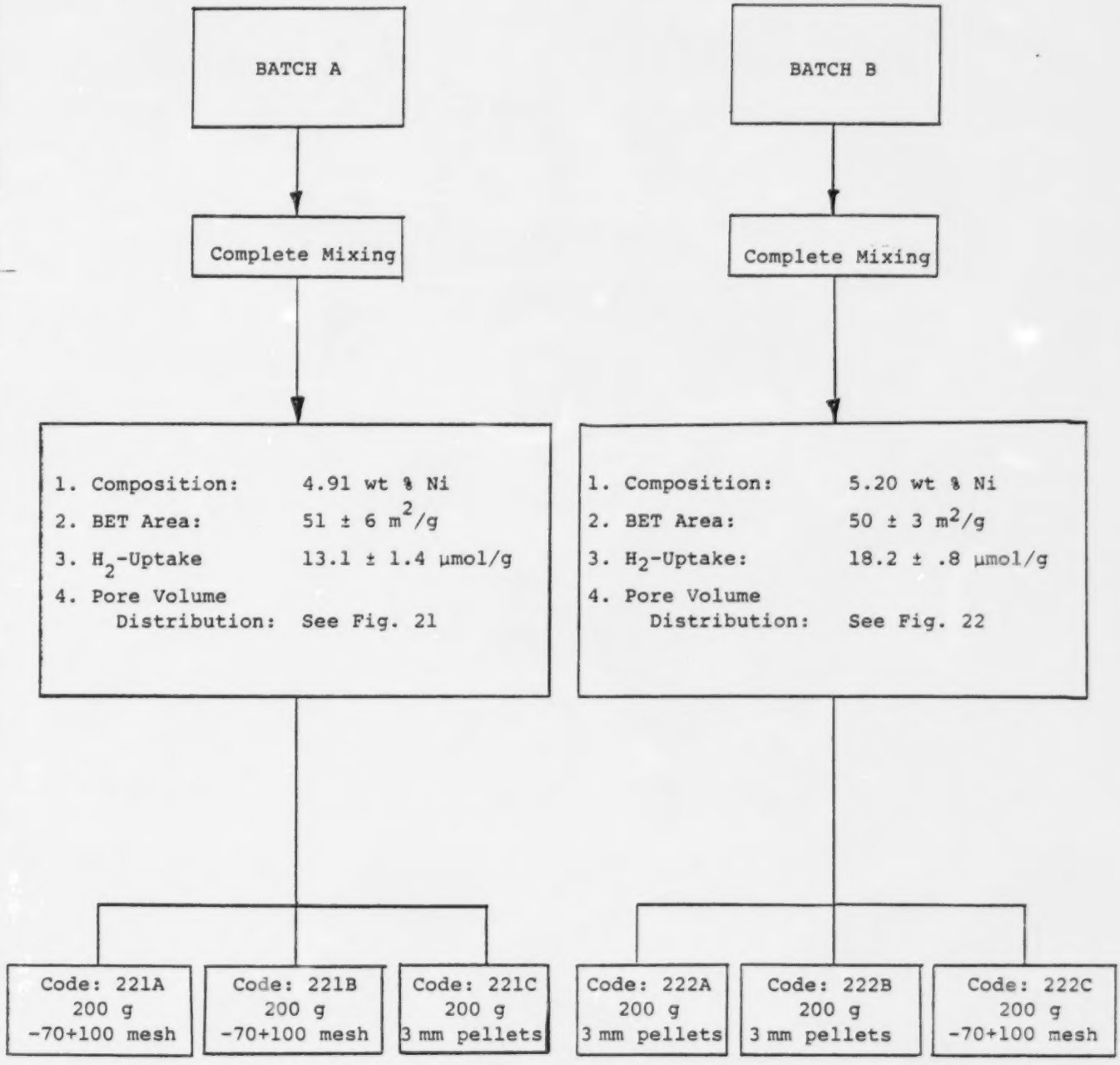
BATCH A
BATCH B
Complete Mixing
Complete Mixing
1. Composition: 4.91 wt % Ni
2. BET Area: 51 ± 6 m²/g
3. H₂-Uptake 13.1 ± 1.4 µmol/g
4. Pore Volume Distribution: See Fig. 21
1. Composition: 5.20 wt % Ni
2. BET Area: 50 ± 3 m²/g
3. H₂-Uptake: 18.2 ± .8 µmol/g
4. Pore Volume Distribution: See Fig. 22
Code: 221A 200 g -70+100 mesh
Code: 221B 200 g -70+100 mesh
Code: 221C 200 g 3 mm pellets
Code: 222A 200 g 3 mm pellets
Code: 222B 200 g 3 mm pellets
Code: 222C 200 g -70+100 mesh

Fig. 20. Preparation and Characterization of the Nickel/Titania Catalyst

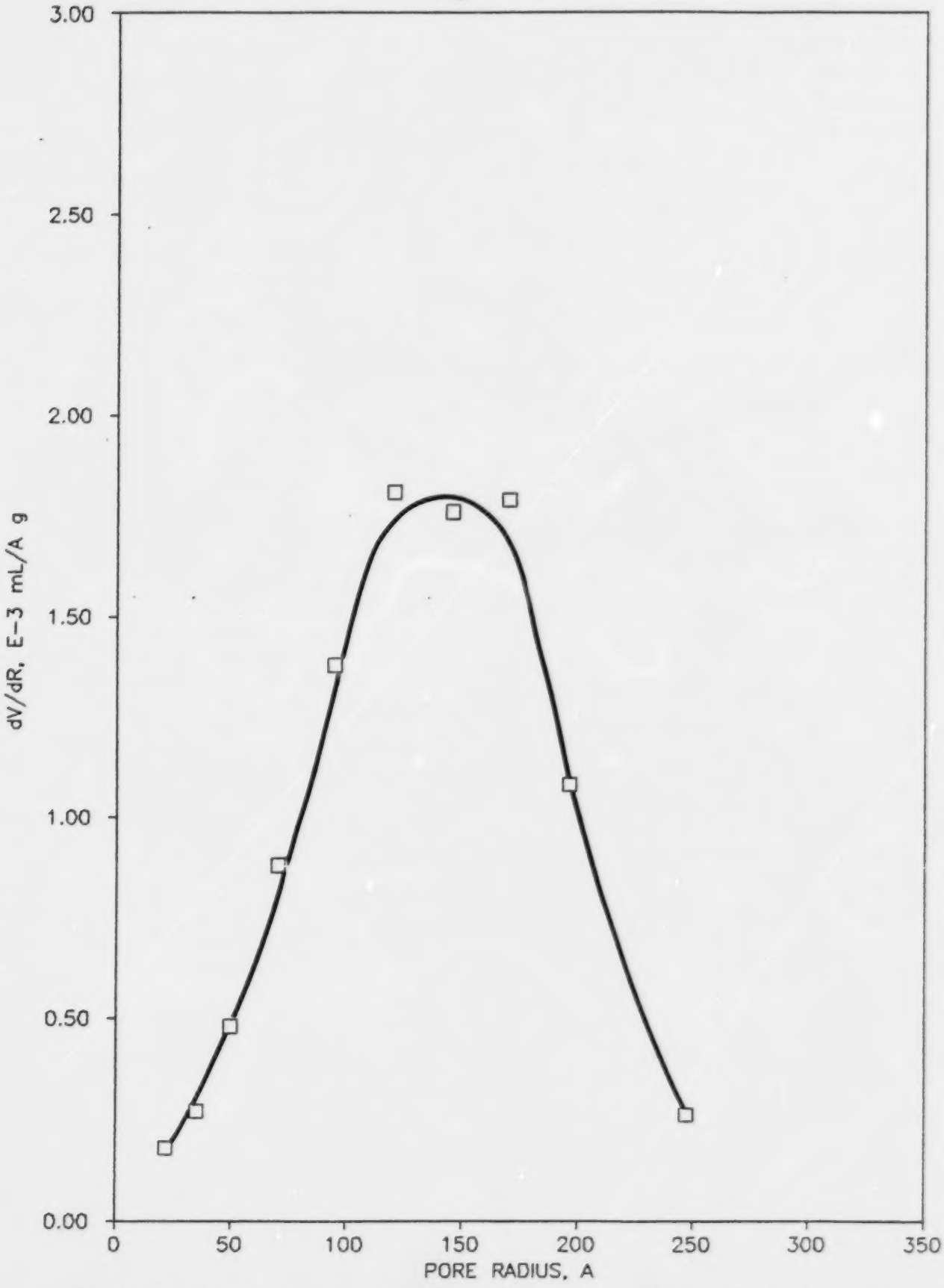

Fig. 21: Pore Volume Distribution of the Nickel/Titania Catalyst (Batch A)

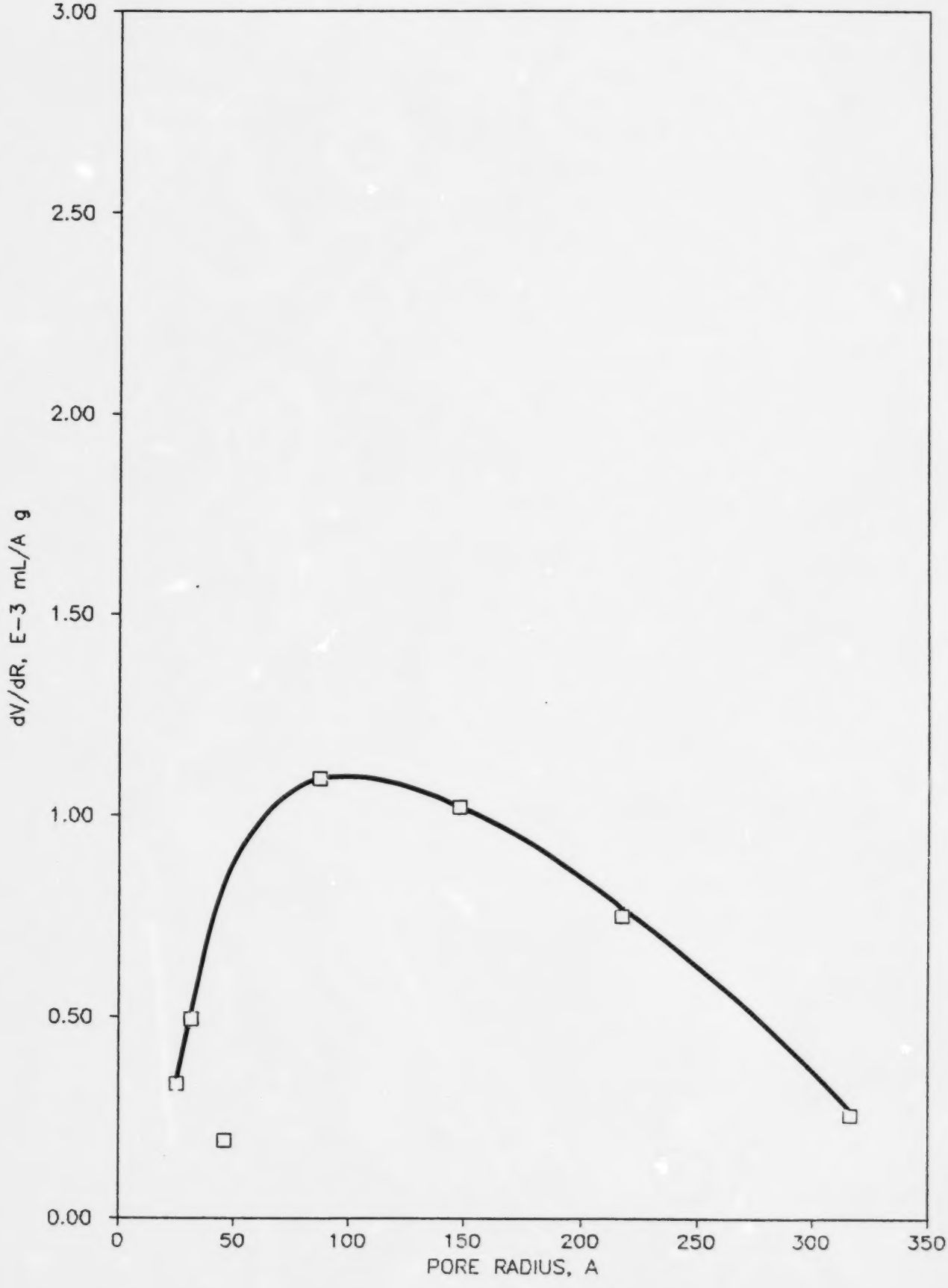

Fig. 22: Pore Volume Distribution of the Nickel/Titania Catalyst (Batch B)

PREPARATION OF NICKEL/ZIRCONIA CATALYST

1. Chemicals and Supports

(i) Nickel Nitrate

For details, see item #1(i) under Preparation of Nickel/Alumina Catalyst.

(ii) Zirconia

For details, see item #1(ii) under Preparation of Iron/Zirconia Catalyst.

A 350 g sample of this support was supplied to the Scientific Authority.

Characteristics of the Support: The following were measured in our laboratory.

1. BET Area: 5.2 m^2/g
2. Pore Volume Distribution: See Fig. 11

2. Preparation of the Catalyst

(i) Drying of the Support

The required amount of zirconia was placed in a large porcelain bowl and dried in a Blue M-Convection oven at 150°C for 24 h. The bowl contained 1392.5 g of zirconia.

(ii) Impregnation

In order to obtain 5 wt% Ni on zirconia support, 367.1g of nickel nitrate was placed in a glass beaker and the beaker placed in the Blue M-Convection oven at 100°C. The nickel nitrate melted, resulting in a homogeneous solution. 30 mL of boiling distilled water was added to the melted nickel nitrate and mixed well. The solution was slowly poured over the zirconia support with gentle and even mixing. Mixing continued for 10 min. This time duration was found to be quite sufficient for complete impregnation. Mixing time was shorter than with other supports on account of the small volume of the zirconia. Impregnation was carried out in a porcelain bowl.

(iii) Drying of the Catalyst

The bowl containing the catalyst from the preceding step (ii) was placed in a fume hood for 48 h. Then it was placed in the Blue M-Convection oven at 90°C for 5 h with intermittent mixin. The catalyst was then allowed to sit in the fume hood for 16 h for complete drying. The bowl was covered with aluminum foil (with a number of holes for the moisture to escape).

(iv) Calcination of the Catalyst

The dried catalyst was kept in the porcelain bowl for the calcination step. The bowls were covered with the same aluminum foil used

for drying of the catalyst. The calcination procedure was the same as that described under 'iron/alumina calcination'.

(v) Chemical Analysis of the Catalyst

The batch was mixed well by putting it into a ball mill without the balls. The mixing continued for 2 h. This gave an extremely well mixed catalyst, so that any sample removed would be completely representative. The Saskatchewan Research Council analyzed the batch for wt % Ni. The catalyst was then sized to give a -70 +100 mesh fraction. BET Surface Area and H_2-Uptake at 120°C were determined from this fraction. Results are shown in Fig. 23.

(vi) Sizing of the Catalyst

(a) Milling and Sizing for -70 +100 Mesh Fraction

The catalyst was carefully milled in a ball mill using metal balls. The resulting product was sieved to obtain the required (600 g) -70 +100 mesh catalyst.

(b) The catalyst left after the required -70 +100 mesh fraction was obtained was made into 3 mm pellets. The catalyst was mixed with enough stearic acid to give 1 wt % stearic acid in the mixture. Care was taken to ensure even mixing. The pellets were made in the same way described in 'iron/alumina catalyst' pelletizing.

(vii) Catalyst Characterization

All characterization took place after mixing and sizing. The final -70 +100 mesh catalyst powder was used for characterization. See Appendix D for information on characterization procedures.

(a) BET Surface Area

Surfaces areas were measured using a Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The value obtained is presented in Fig. 23.

(b) Pore Volume Distribution

The pore volume distribution was determined from the nitrogen desorption isotherm using the Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D. The results are presented in Fig. 24.

(c) H_2-Uptake at 120°C

The Micromeritics Surface-Area Pore-Volume Analyzer, Model 2100D was used.

An adsorption isotherm was obtained at 120°C and then the curve was extrapolated to 0 mm Hg to obtain the H_2-uptake value. The value obtained is given in Fig. 23.

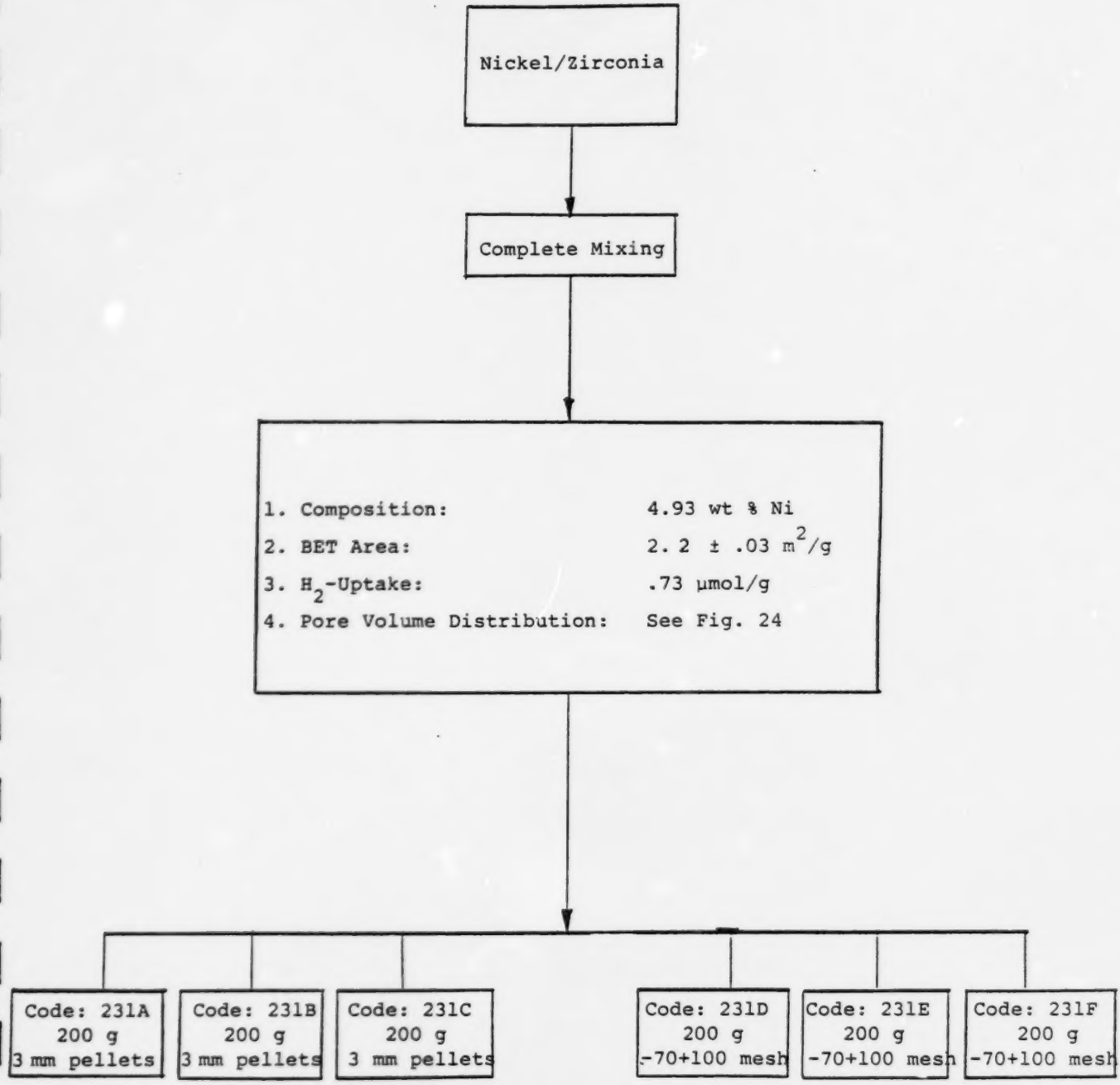
Nickel/Zirconia
Complete Mixing
1. Composition: 4.93 wt % Ni
2. BET Area: 2.2 ± .03 m²/g
3. H₂-Uptake: .73 µmol/g
4. Pore Volume Distribution: See Fig. 24
Code: 231A 200 g 3 mm pellets
Code: 231B 200 g 3 mm pellets
Code: 231C 200 g 3 mm pellets
Code: 231D 200 g -70+100 mesh
Code: 231E 200 g -70+100 mesh
Code: 231F 200 g -70+100 mesh

Fig. 23. Preparation and Characterization of the Nickel/Zirconia Catalyst

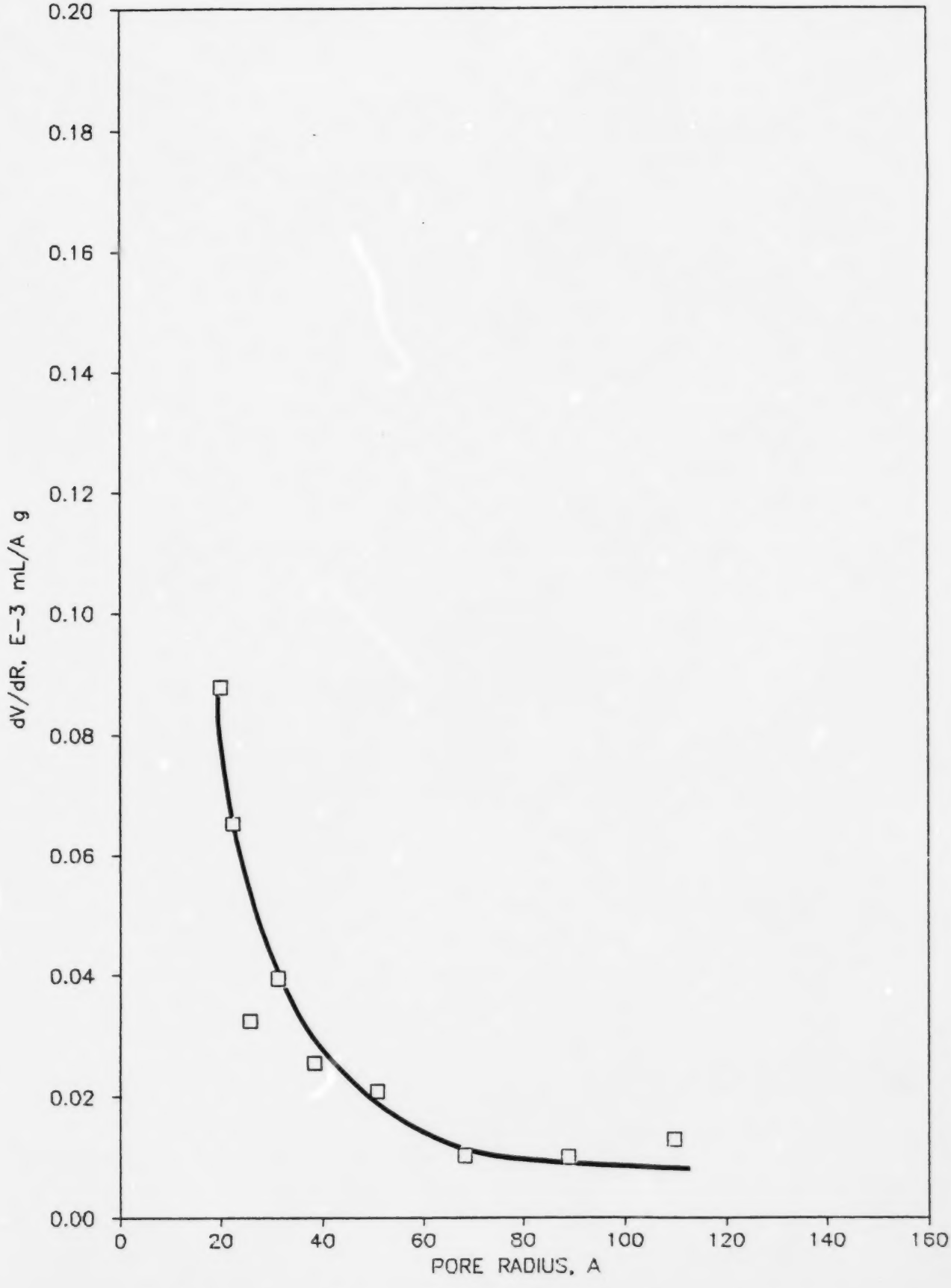

Fig. 24: Pore Volume Distribution of the Nickel/Zirconia Catalyst

GENERAL COMMENTS

In order to manufacture these catalysts at the kg-scale, we faced a number of problems. These are discussed below:

1. **Iron/alumina and nickel/alumina catalysts:**

   A major problem was in the sizing of the -70+100 mesh fraction. Sieving consumed excessively large amounts of time.

2. **Iron/zirconia and nickel/zirconia catalysts:**

   (i) Zirconia support has a much smaller pore volume than the other three supports. Hence, only a small amount of the impregnating salt solution was needed. Also, the solution does not wet the zirconia support fully. These problems were overcome by melting the iron and nickel nitrates at 50-60°C and then impregnating the zirconia support while the solution was still warm. This process ensured complete wetting of the support, and hence complete impregnation.

   (ii) Another intriguing problem encountered was that of color change of the catalyst mass during the drying stage. When the iron/zirconia catalyst was dried in the oven at 90°C, it was found that a part of the catalyst changed its color from pale-yellowish brown to purple. We checked this behavior with our colleagues from Chemistry, but no satisfactory explanation could be obtained. After a number of trials (all time consuming) it was found that if the catalyst was air dried initially and then calcined, no color change was observed. This technique was then used for the preparation of the catalysts (iron/zirconia and nickel/zirconia).

3. Details of BET, H_2 - Chemisorption and Pore Size Distribution

Micrometrics surface Area, Pore Volume Analyzer Model 2100D was used for these measurements. Details for these measurements are given in the manual for this instrument. Also, the pertinent details are given in Appendix D.

APPENDIX A

Calculations of Catalyst Chemical Composition

Fe/Al_2O_3

We want 5 wt % Fe on 95 wt % Al_2O_3 (ie. 5 wt % Fe and 50.28 wt % Al).

The ratio of Al/Ni that we want is 50.28/5 = 10.06.

SRC analysis reports: Al = 46.0 Fe = 4.70

Al/Fe ratio = 46.0/4.70 = 9.78

10.06/9.78 x 5 wt % Ni = 5.12 wt % Ni

wt % Al_2O_3 = 94.88 (see Fig. 2)

Fe/SiO_2

We want 5 wt % Fe on 95 wt % SiO_2 (ie. 5 wt % Fe and 44.41 wt % Si).

The ratio of Si/Fe that we want is 44.41/5 = 8.88.

SRC analysis reports: Si = 41.2 Fe = 4.73

Si/Fe ratio = 41.2/4.73 = 8.71

8.88/8.71 x 5 wt % Fe = 5.10 wt % Fe

wt % SiO_2 = 94.20 (see Fig. 5)

Fe TiO_2

We want 5 wt % Fe on 95 wt % TiO_2 (ie. 5 wt % Fe on 56.94 wt % Ti).

The ratio of Ti/Fe that we want is 56.94/5 = 11.39.

SRC analysis reports: For Batch A: Ti = 63, Fe = 5.7
For Batch B: Ti = 56, Fe = 5.0

For Batch A, Ti/Fe ratio = 63/5.7 = 11.05

11.39/11.05 x 5 wt % Fe = 5.15 wt % Fe

wt % TiO_2 = 94.85 (see Fig. 8)

For Batch B, Ti/Fe ratio = 56/5.0 = 11.20

11.39/11.20 x 5 wt % Fe = 5.08 wt % Fe

wt % TiO_2 = 94.92 (see Fig. 8)

Fe ZrO_2

We want 5 wt % Fe on 95 wt % ZrO_2 (ie. 5 wt % Ni on 70.33 wt % Zr).

The ratio of Zr/Fe that we want is 70.33/5 = 14.07.

SRC analysis reports Fe = 5.05, Zr = 70.2

Zr/Fe ration = 70.2/5.05 = 13.90

14.07/13.90 x 5 wt% Fe = 5.06 wt % Fe

wt % ZrO_2 = 94.95 (see Fig. 12)

Ni/Al_2O_3

We want 5 wt % Ni on 95 wt % Al_2O_3 (ie. 5 wt% Ni and 50.28 wt % Al).

The ratio of Al/Ni that we want is 50.28/5 = 10.06.

SRC analysis reports: For Batch A, Al = 44.7, Ni = 4.4
For Batch B, Al = 4.75, Ni = 4.8
For Batch C, Al = 45, Ni = 4.95

For Batch A, Al/Ni ratio = 44.7/4.4 = 10.16

10.06/10.10 x 5 wt % Ni = 4.95 wt % Ni

wt % Al_2O_3 = 95.05 (see Fig. 14)

For Batch B, Al/Ni ratio = 47.5/4.8 = 9.90

10.06/9.90 x 5 wt % Ni = 5.08 wt % Ni

wt % Al_2O_3 = 94.92 (see Fig. 14)

For Batch C, Al/Ni ratio = 45/4.95 = 9.09

10.06/9.09 x 5 wt % Ni = 5.53 wt % Ni

wt % Al_2O_3 = 94.47 (see Fig. 14)

Ni/SiO_2

We want 5 wt % Ni on 95 wt % SiO_2 (ie. 5 wt % Ni and 44.41 wt % Si)

The ratio of Si/Ni that we want is 44.41/5 = 8.88.

SRC analysis reports: For Batch A, Si = 39, Ni = 4.14
For Batch B, Si = 39, Ni = 4.15

For Batch A, Si/Ni ratio = 39/4.14 = 9.42

8.88/9.42 x 5 wt % Ni = 4.71 wt % Ni

wt % SiO_2 = 95.29 (see Fig. 17)

For Batch B, Si/Ni ratio = 39/4.15 = 9.40

8.88/9.42 x 5 wt % Ni = 4.72 wt % Ni

wt % SiO_2 = 95.28 (see Fig. 17)

Fig. 22: Pore Volume Distribution of the Nickel/Titania Catalyst (Batch B)

Ni TiO_2

We want 5 wt % Ni on 95 wt % TiO_2 (ie. 5 wt % Ni on 56.94 wt % Ti).

The ratio of Ti/Ni that we want is 56.94/5 = 11.39.

SRC analysis reports: For Batch A, Ti = 58, Ni = 5
For Batch B, Ti = 58, Ni = 5.3

For Batch A, Ti/Ni ratio = 58/5 = 11.60

11.39/11.60 x 5 wt % Ni = 4.91 wt % Ni

wt % TiO_2 = 95.09 (see Fig. 20)

For Batch B, Ti/Ni ratio = 58/5.3 = 10.94

11.39/10.94 x 5 wt % Ni = 5.20 wt % Ni

wt % TiO_2 = 4.80 (see Fig. 20)

Ni/ZrO_2

We want 5 wt % Ni on 95 wt % ZrO_2 (ie. 5 wt % Ni and 70.33 wt % Zr).

The ratio of Zr/Ni that we want is 70.33/5 = 14.07.

SRC analysis reports Ni = 4.98, Zr = 71

Zr/Ni ratio = 71/4.98 = 14.26

14.07/14.26 x 5 wt % Ni = 4.93 wt % Ni

wt % ZrO_2 = 95.07 (see Fig. 23)

APPENDIX B

BET Graphs Used For Determination of Surface Area

For a detailed derivation of the BET Graphs and its theory, see Instruction manual for the Accusorb 2100E.*

P_2 = Pressure of gas after adsorbtion has taken place

Ps = Saturation pressure of gas

V = Volume of gas adsorbed

X = P_2/Ps

*Micromeritics
5680 Goshen Springs Road
Norcross, Georgia 30093
U.S.A.

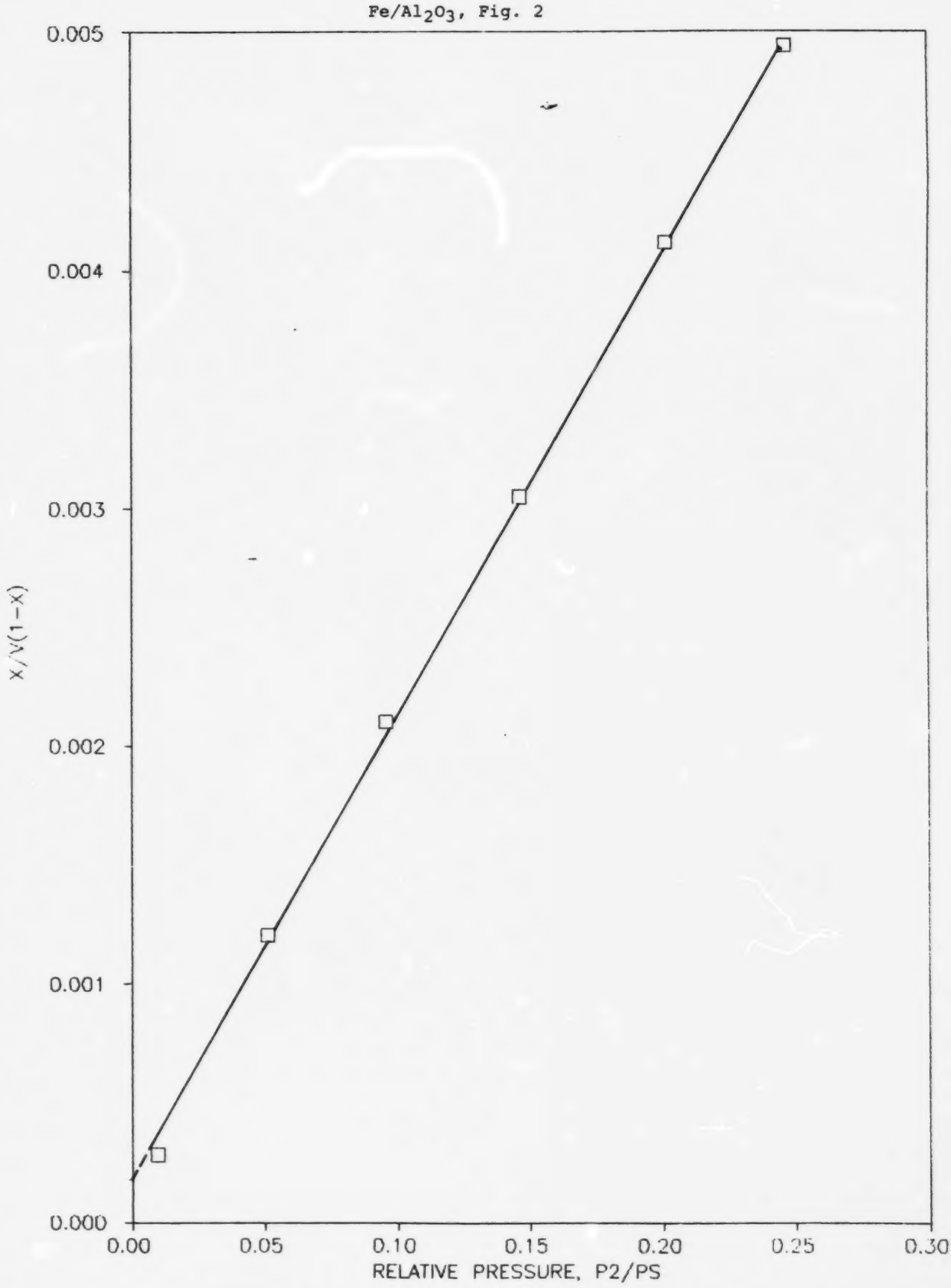

Fig. B1 BET Graph of the Iron/Alumina Catalyst

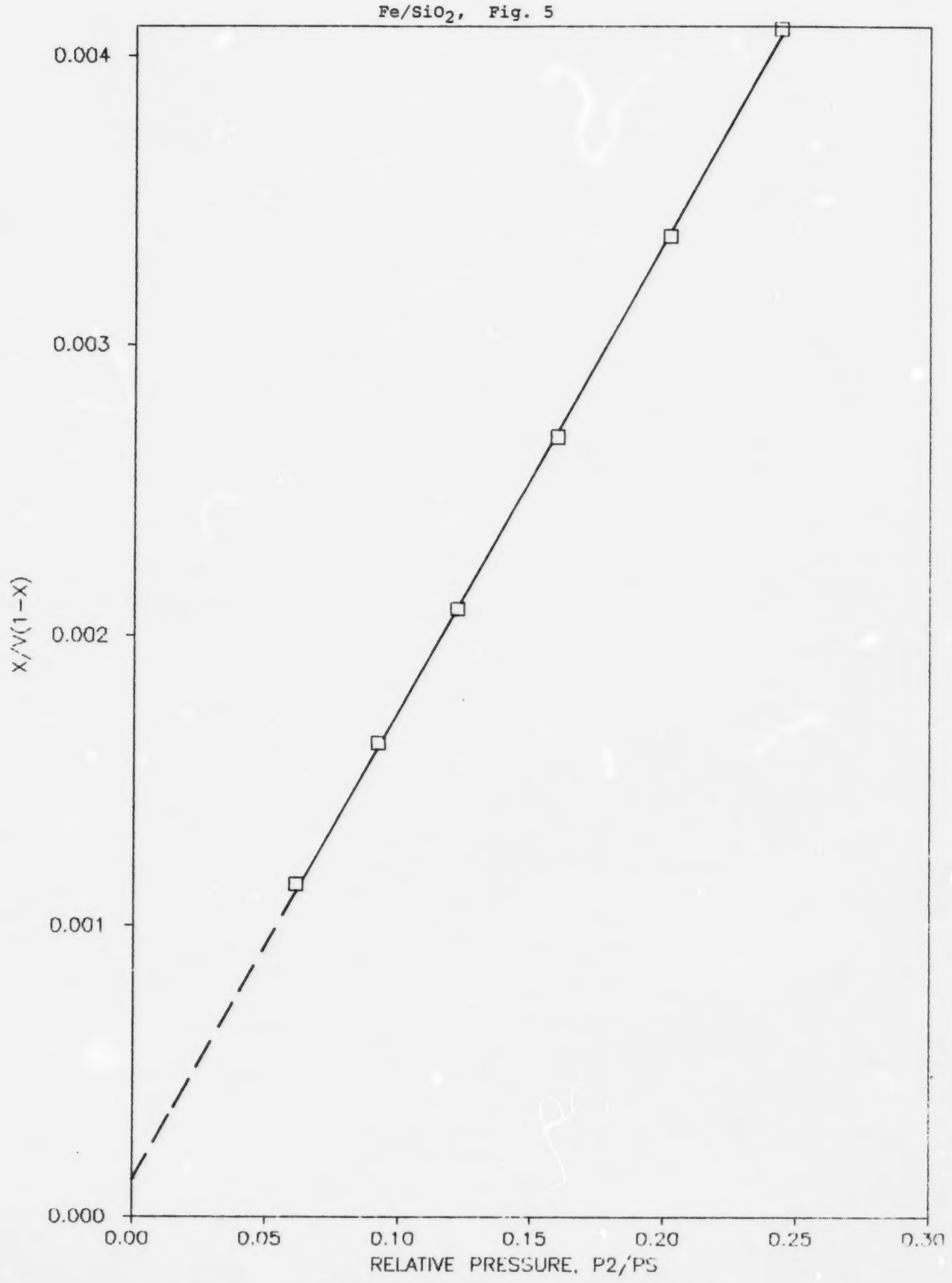

Fig. B2 BET Graph of the Iron/Silica Catalyst

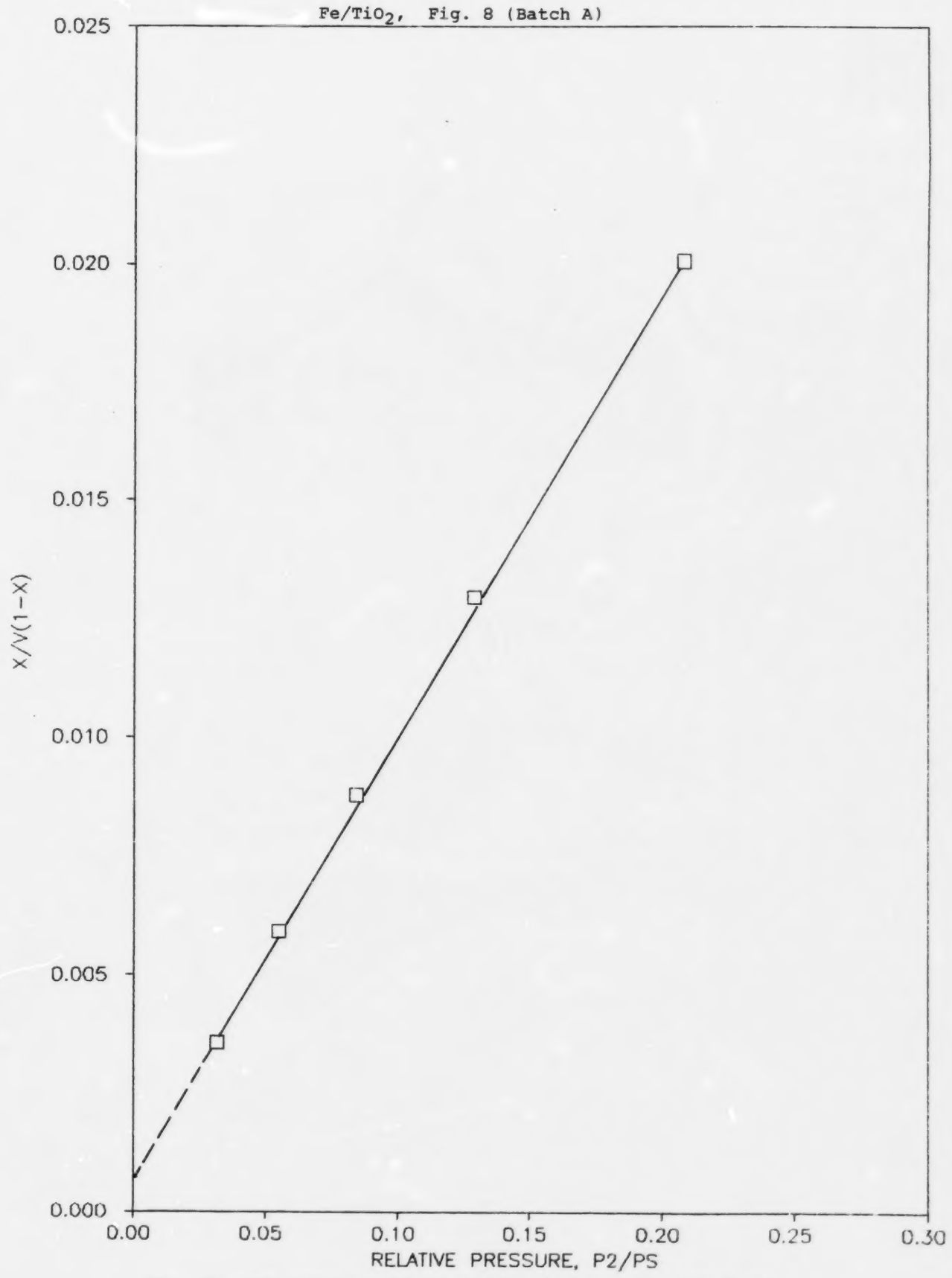

Fig. B3 BET Graph of the Iron/Titania Catalyst (Batch A)

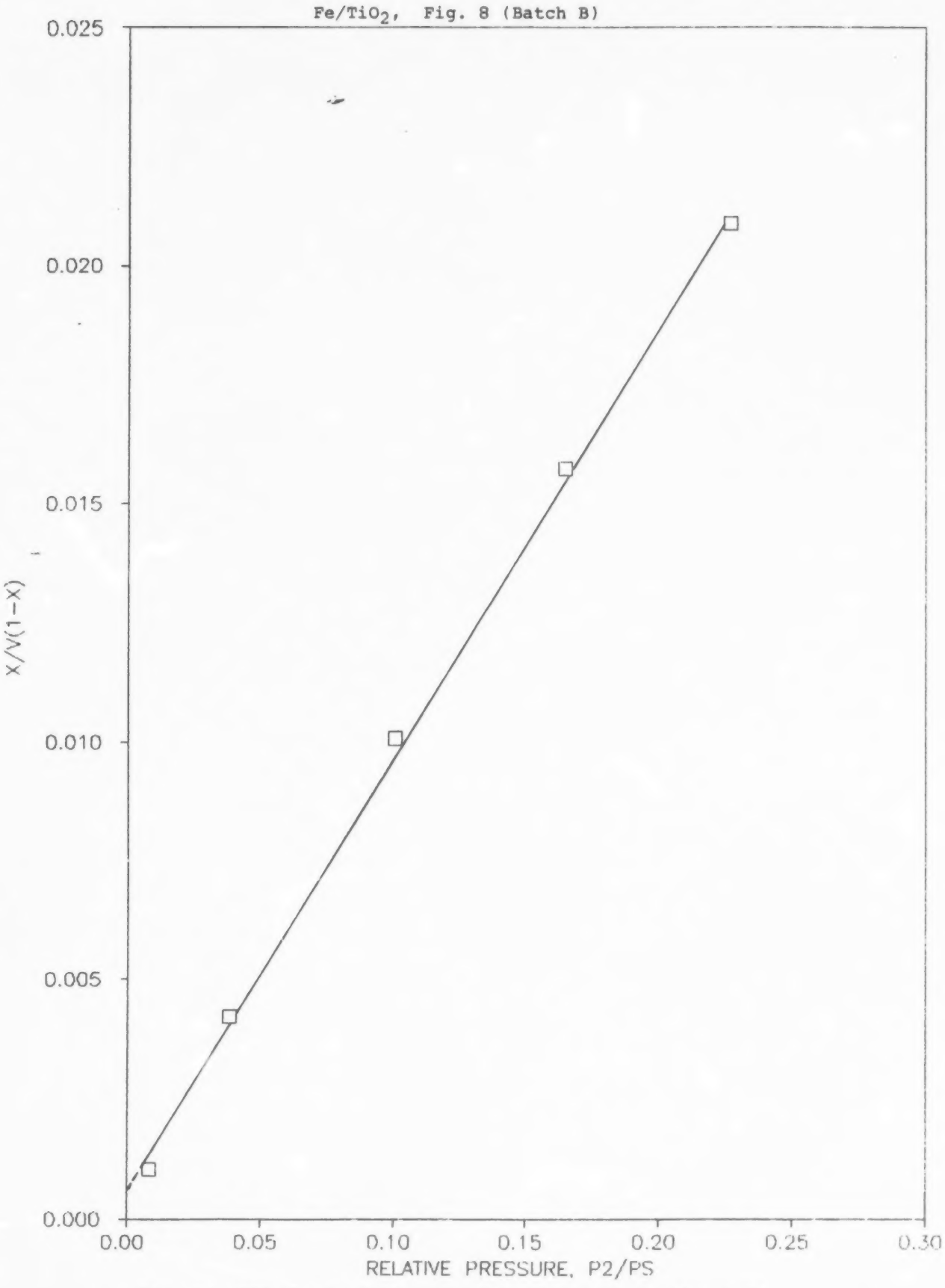

Fig. B4 BET Graph of the Iron/Titania Catalyst (Batch B)

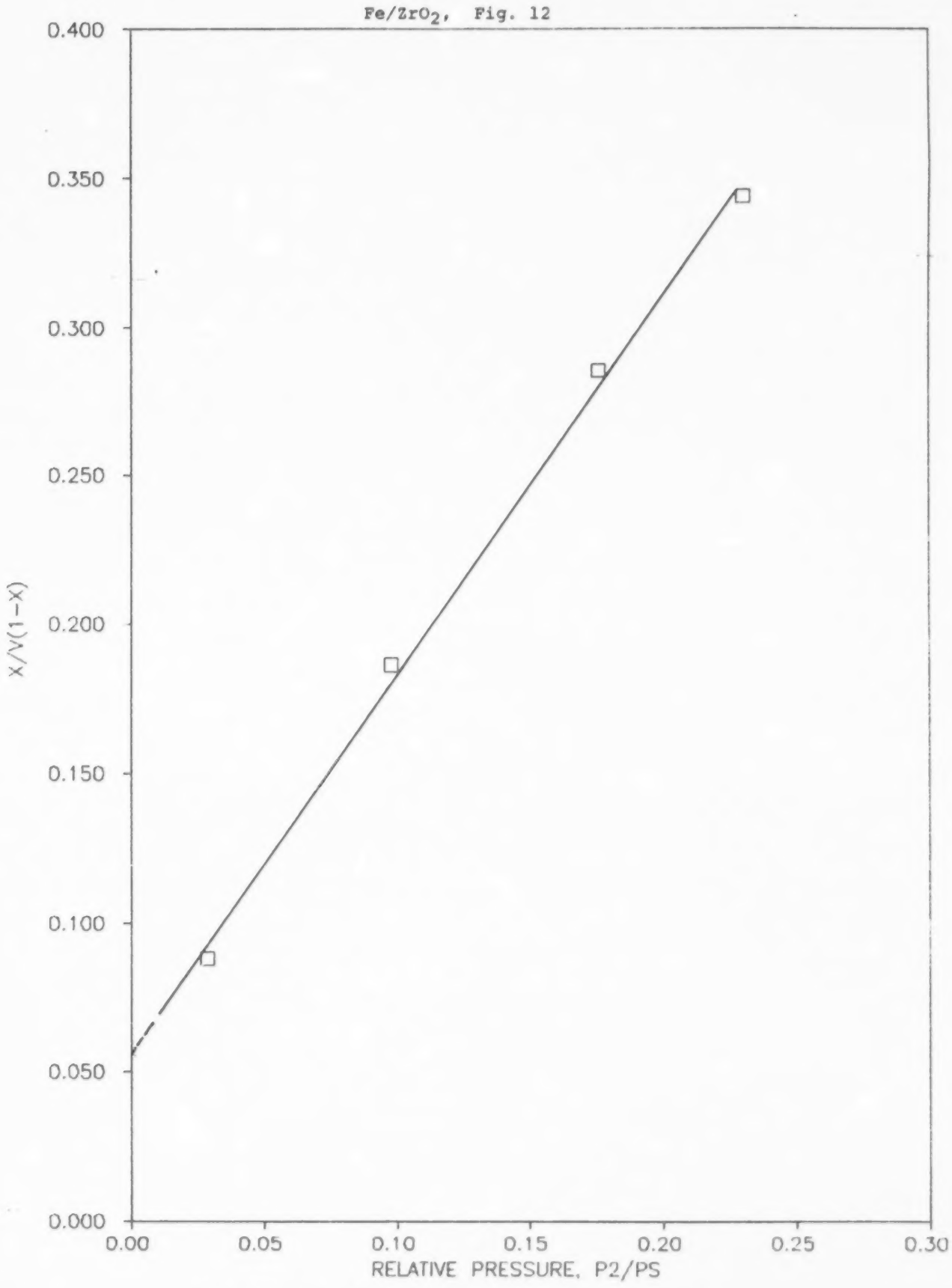

Fig. B5 BET Graph of the Iron/Zirconia Catalyst

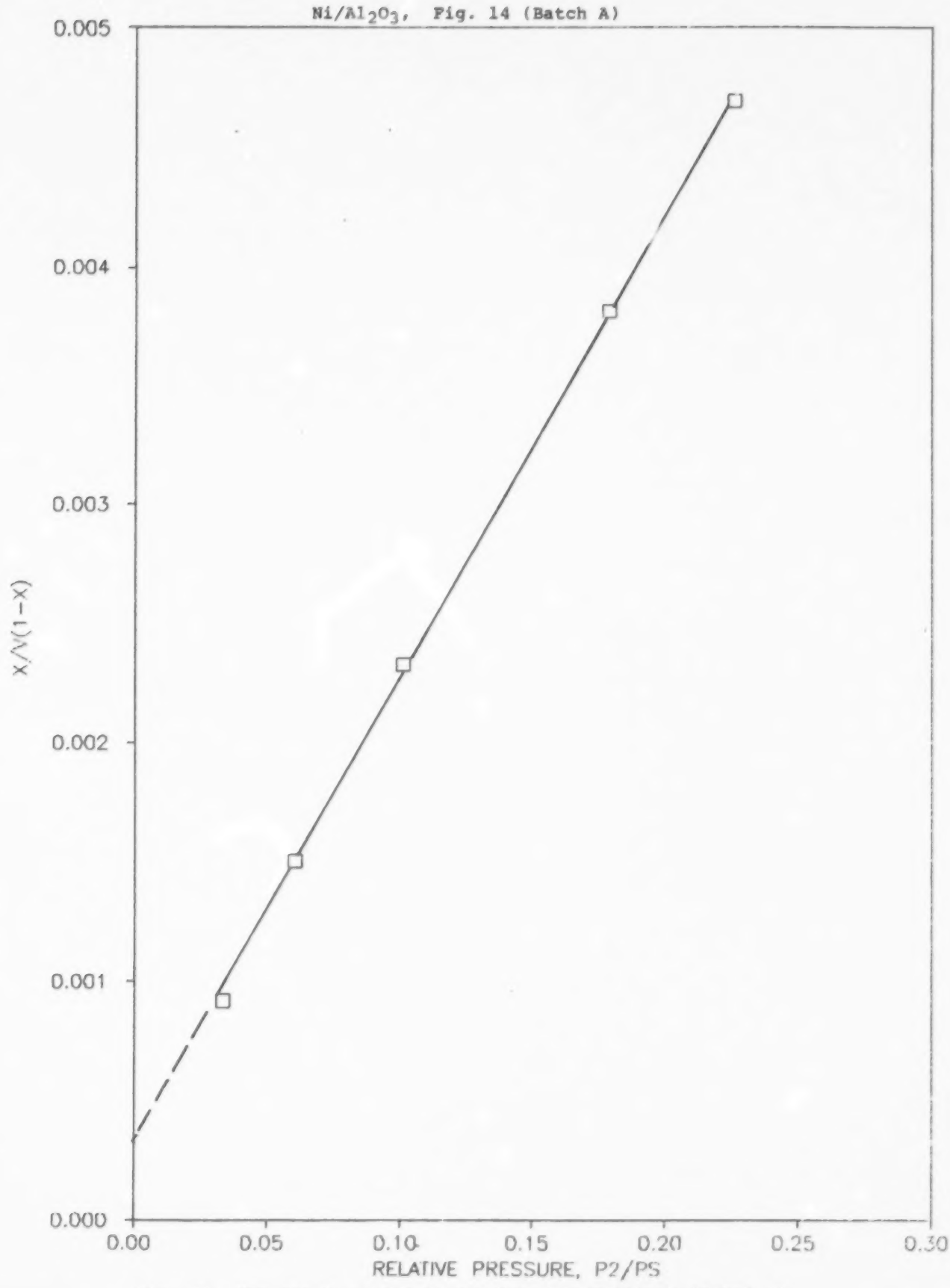

Fig. B6 BET Graph of the Nickel/Alumina Catalyst (Batch A)

Ni/Al_2O_3, Fig. 14 (Batch B)

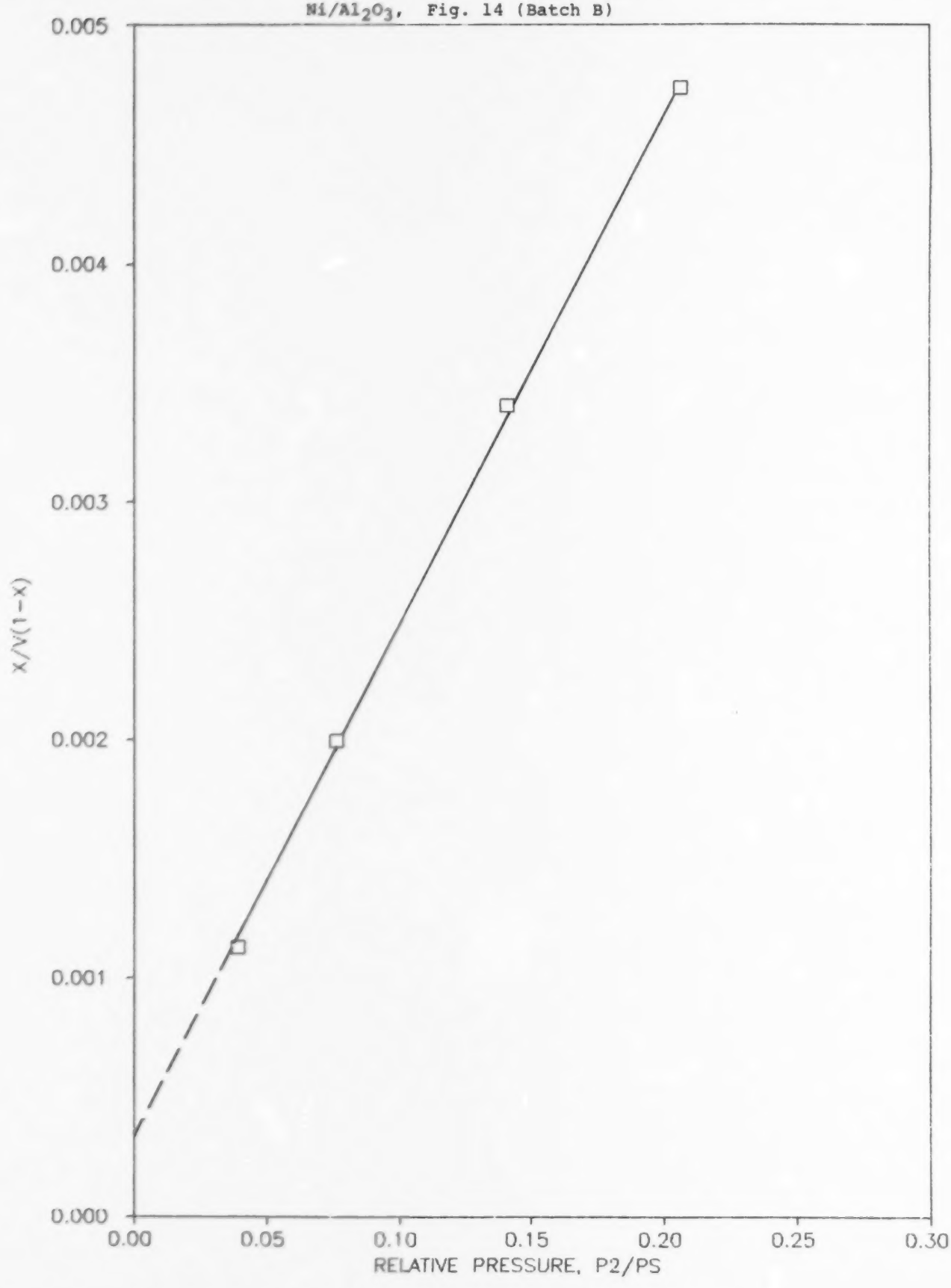

Fig. B7 BET Graph of the Nickel/Alumina Catalyst (Batch B)

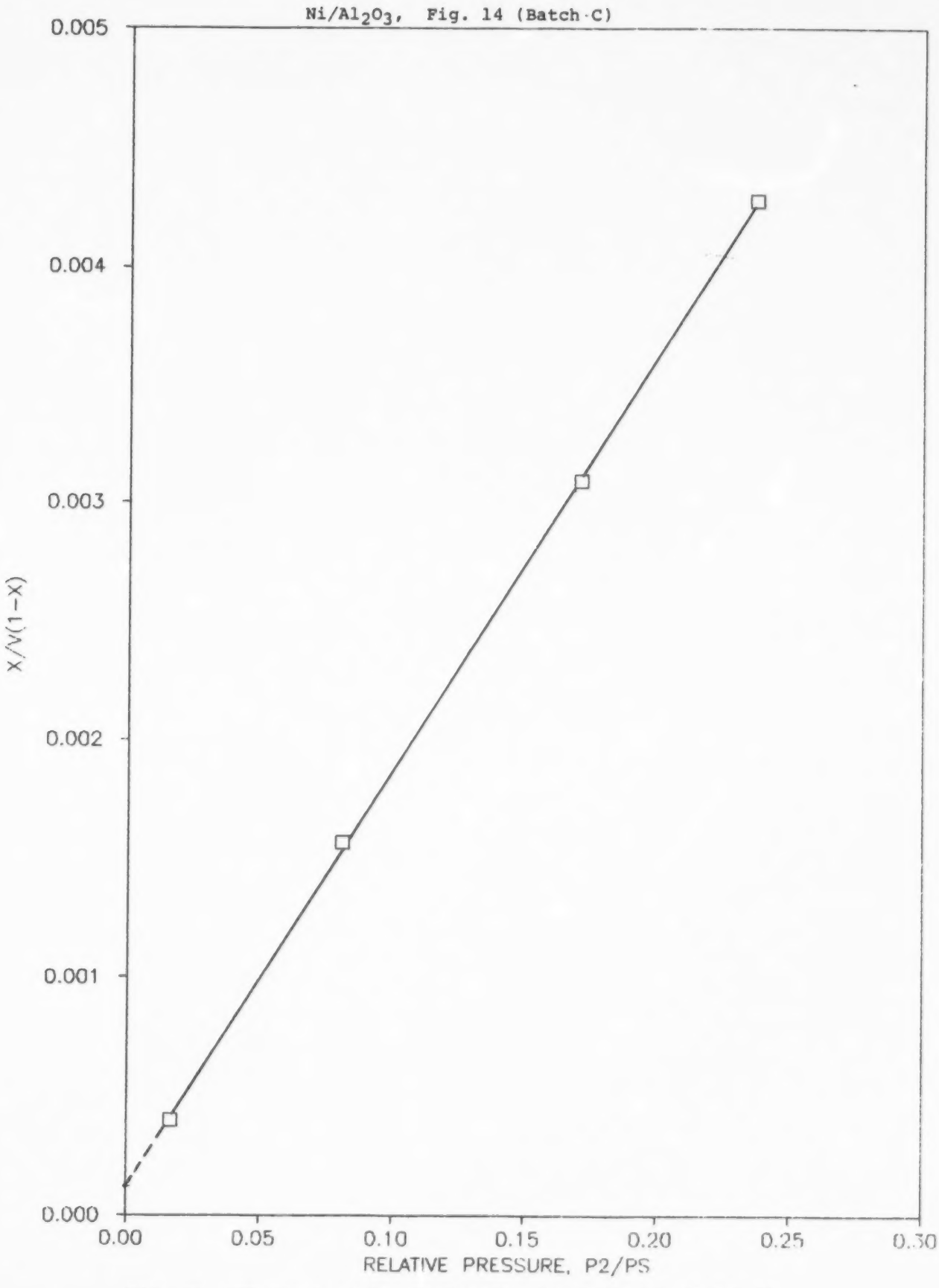

Fig. B8 BET Graph of the Nickel/Alumina Catalyst (Batch C)

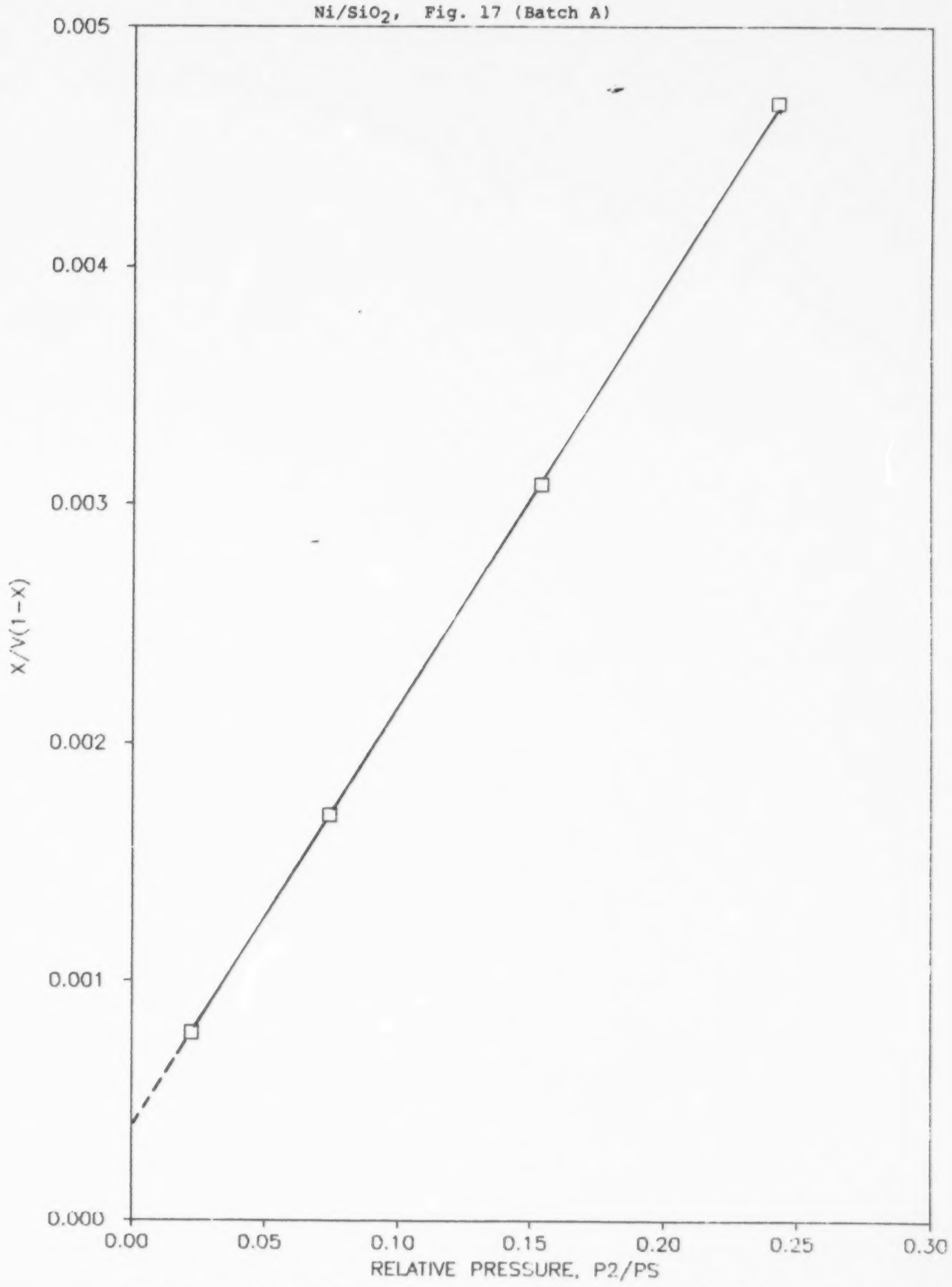

Fig. B9 BET Graph of the Nickel/Silica Catalyst (Batch A)

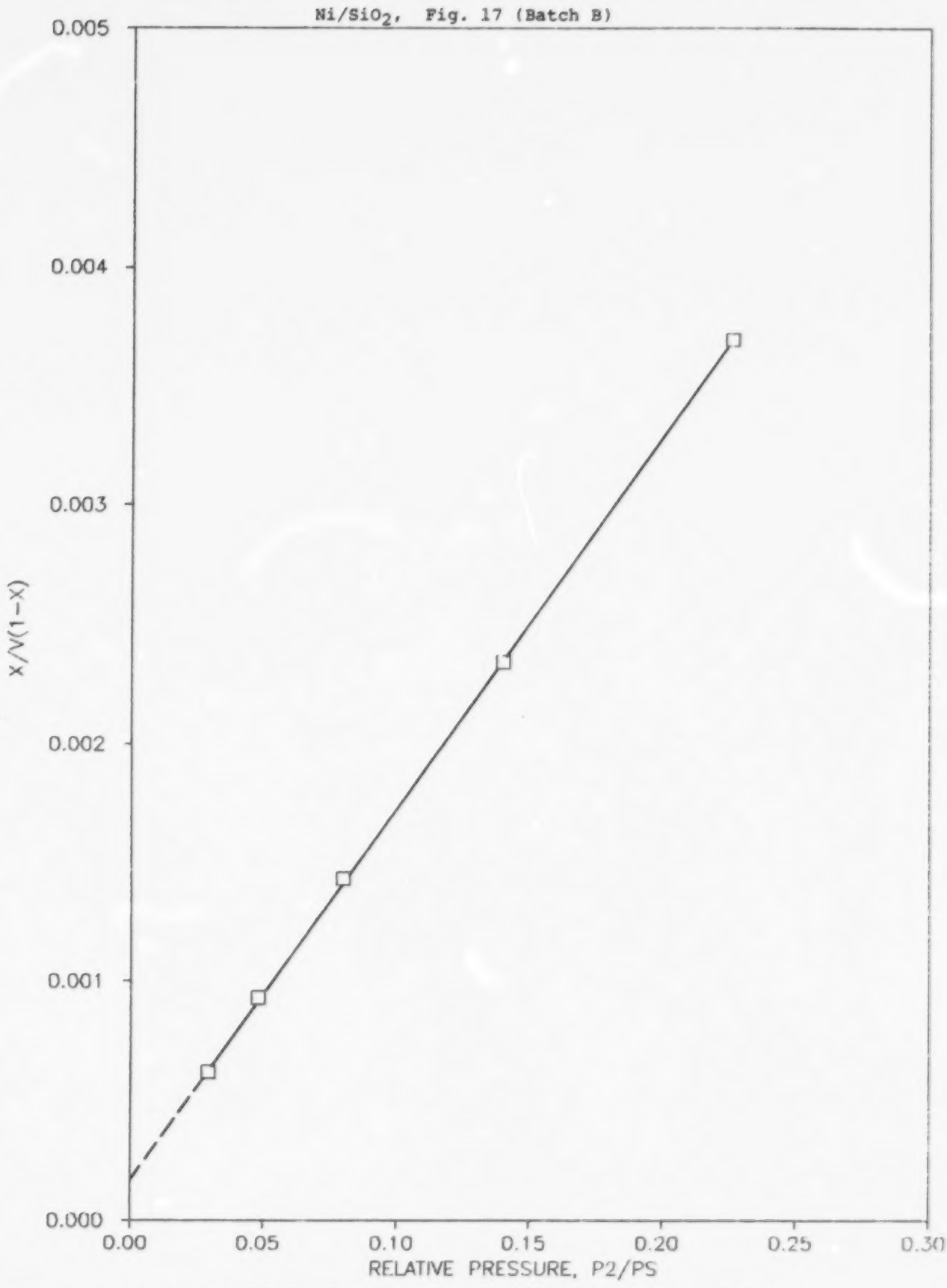

Fig. B10 BET Graph of the Nickel/Silica Catalyst (Batch B)

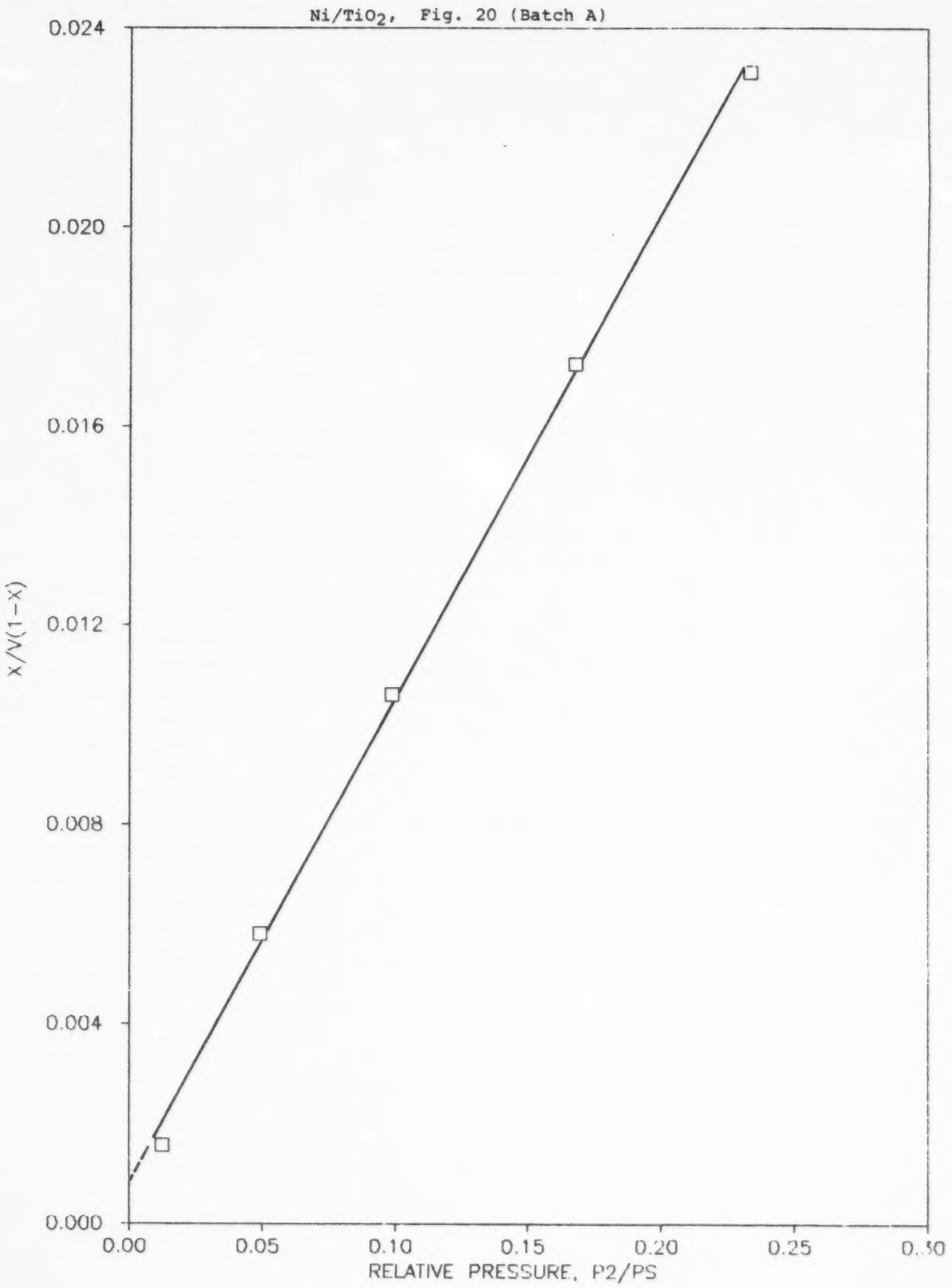

Fig. B11 BET Graph of the Nickel/Titania Catalyst (Batch A)

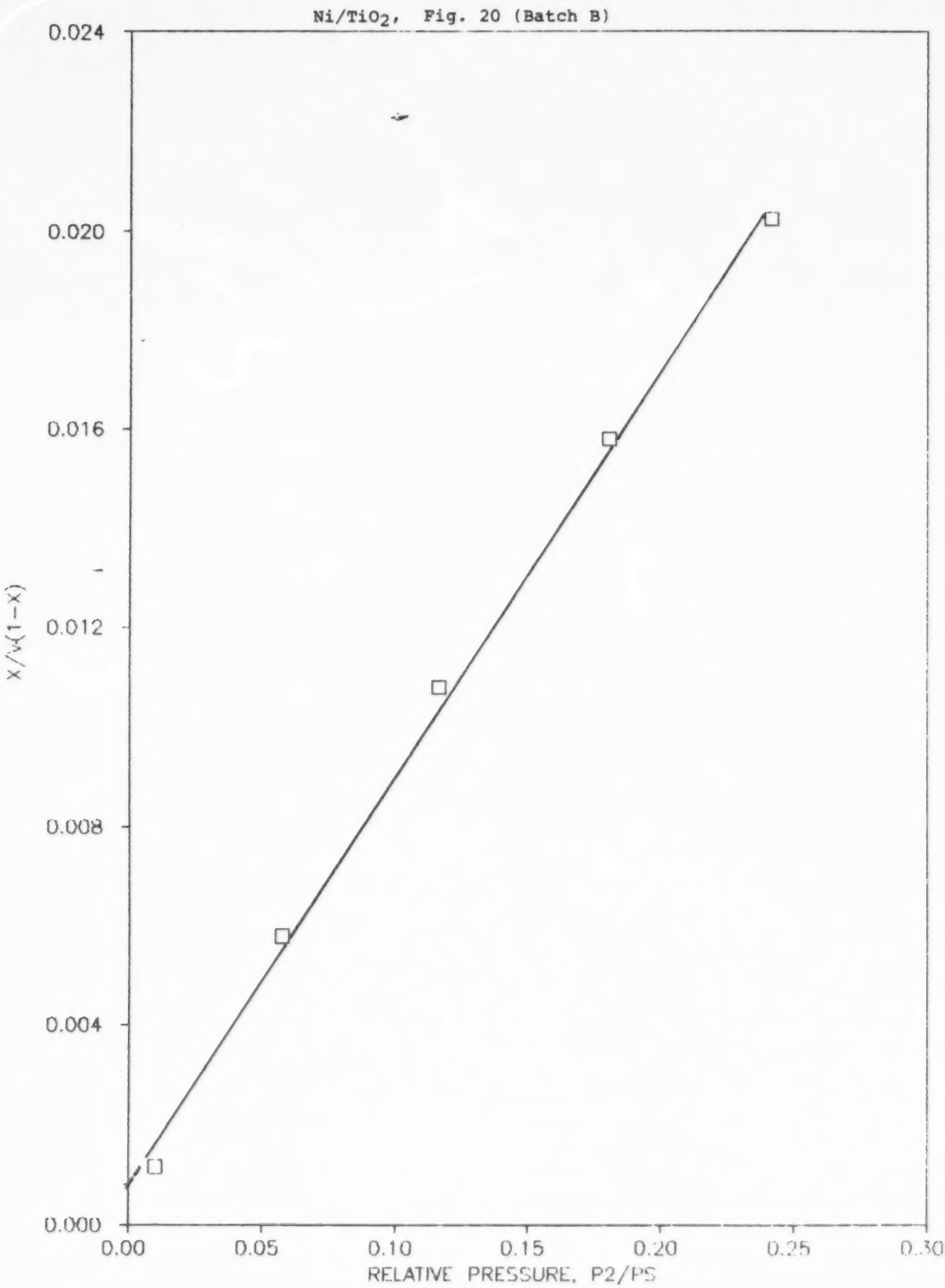

Fig. B12 BET Graph of the Nickel/Titania Catalyst (Batch B)

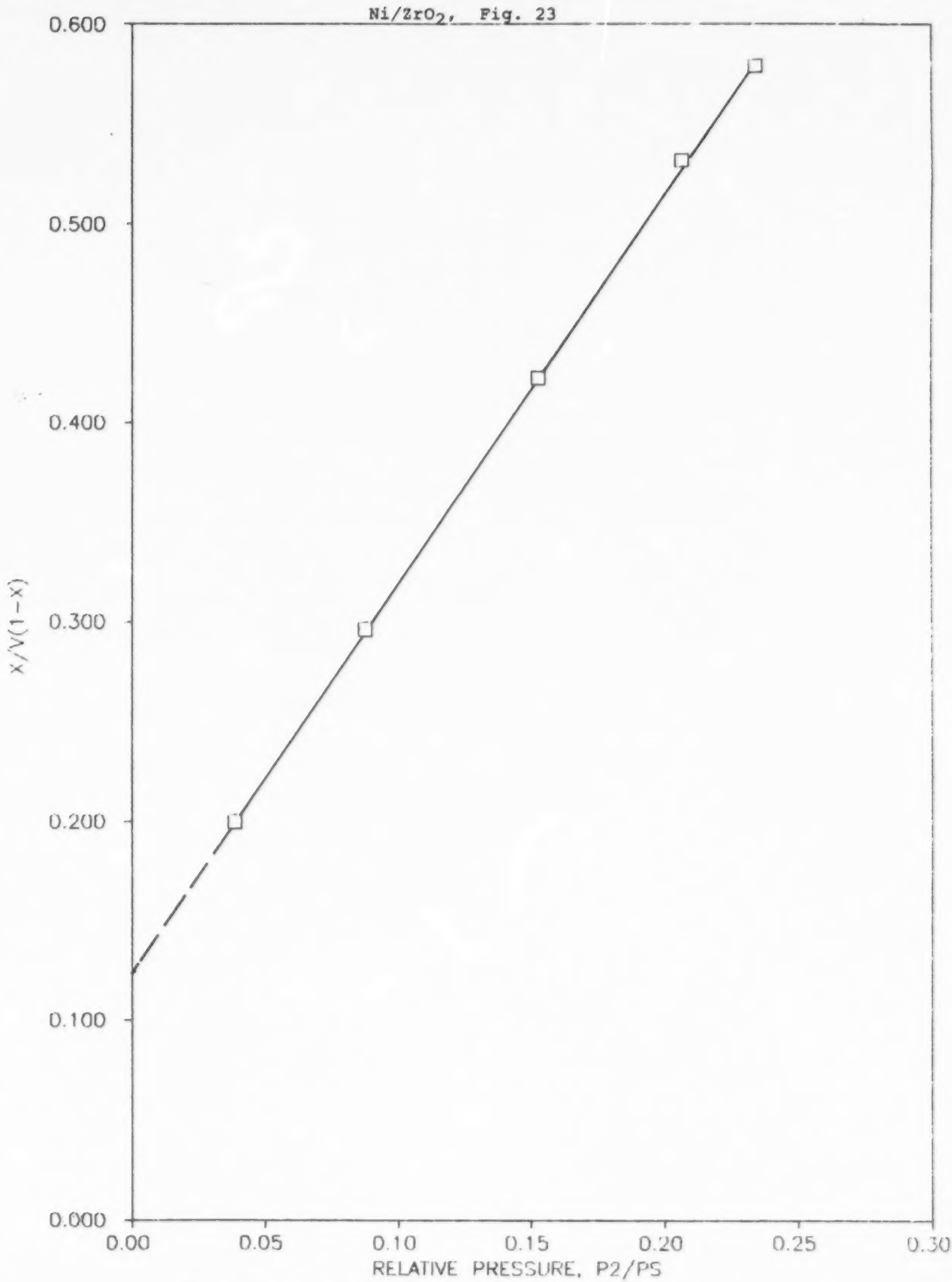

Fig. B13 BET Graph of the Nickel/Zirconia Catalyst

APPENDIX C

Graphs Used For Determination of
H_2-Uptake Values

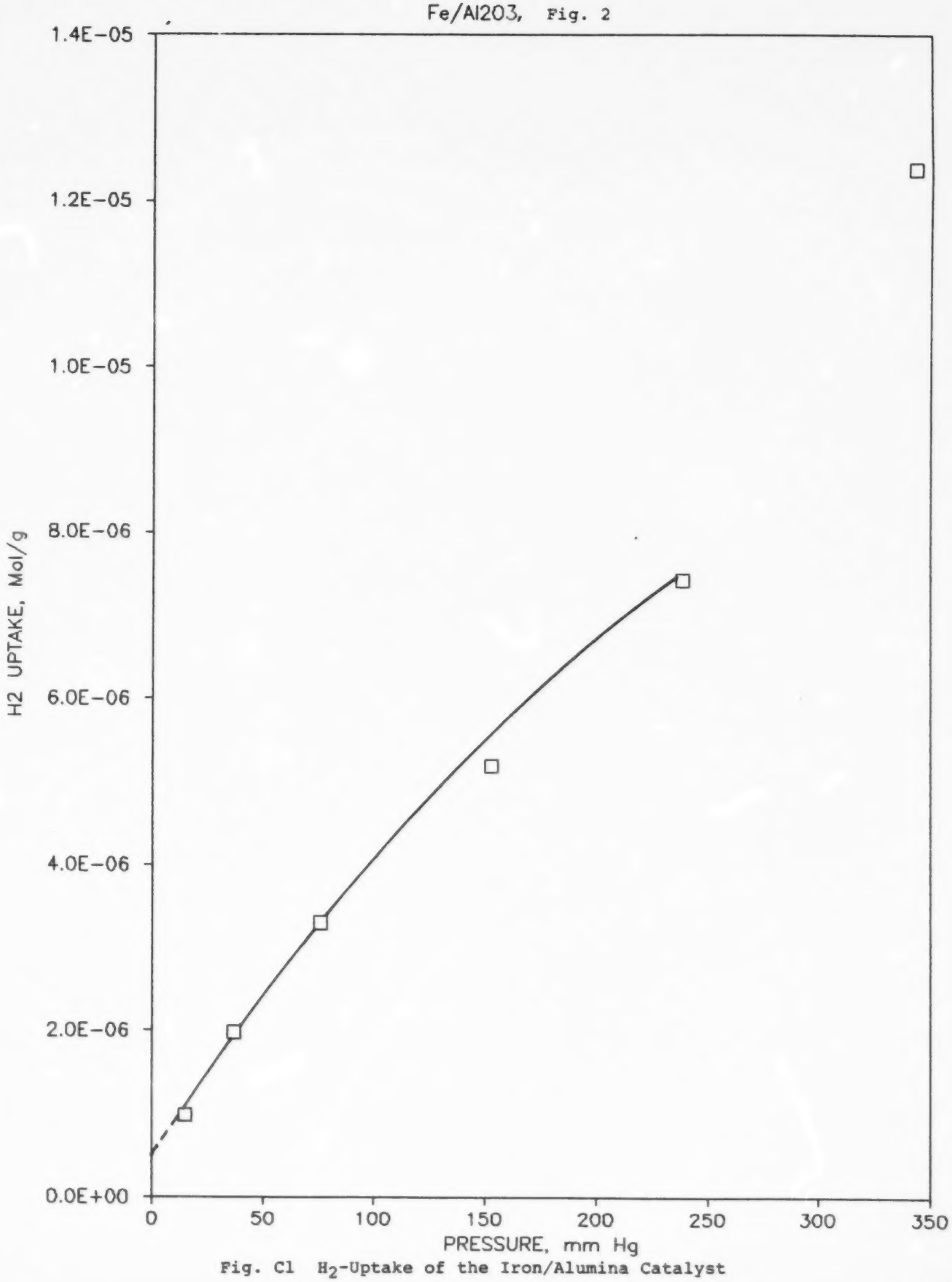

Fig. C1 H_2-Uptake of the Iron/Alumina Catalyst

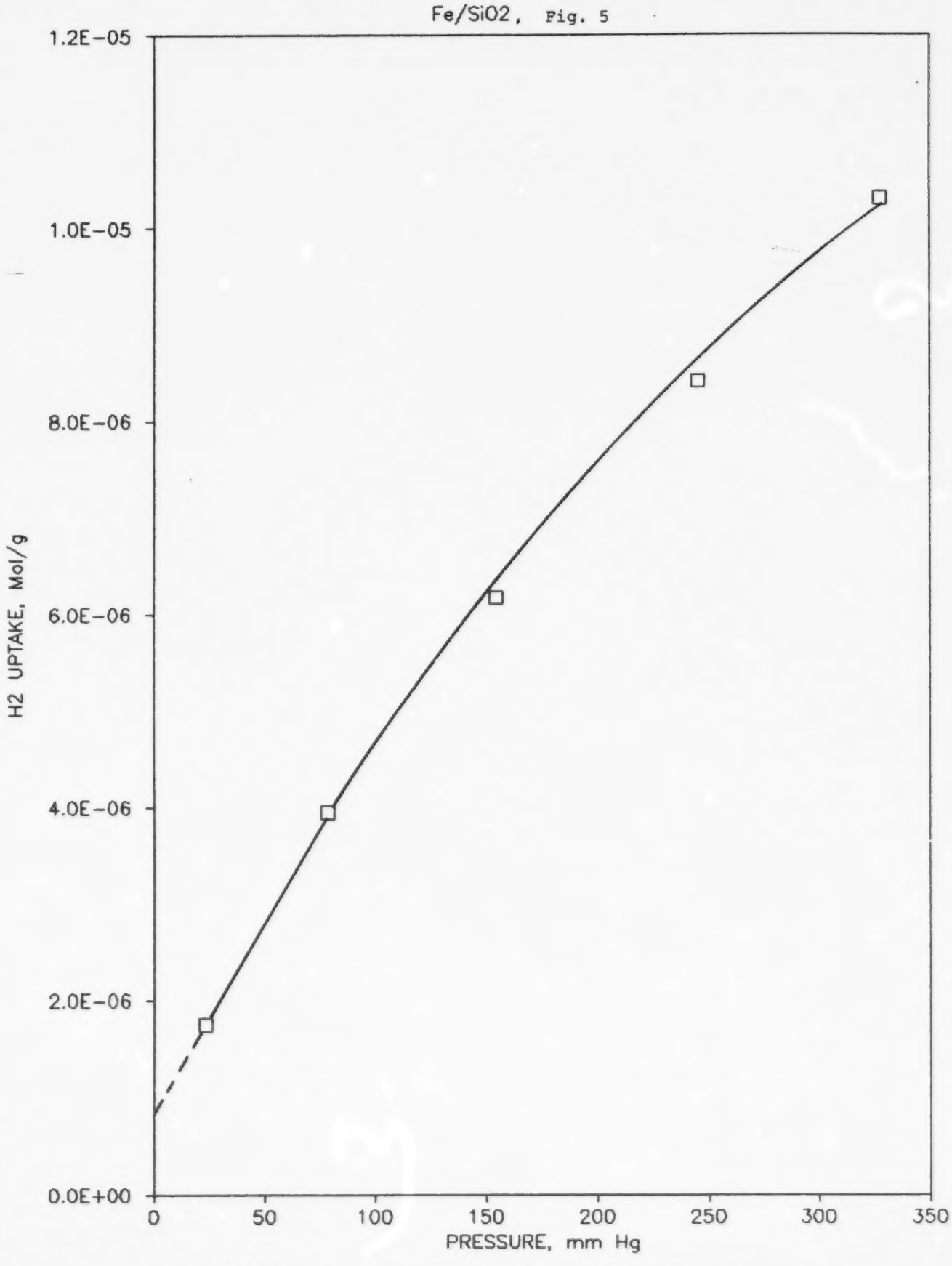

Fig. C2 H_2-Uptake of the Iron/Silica Catalyst

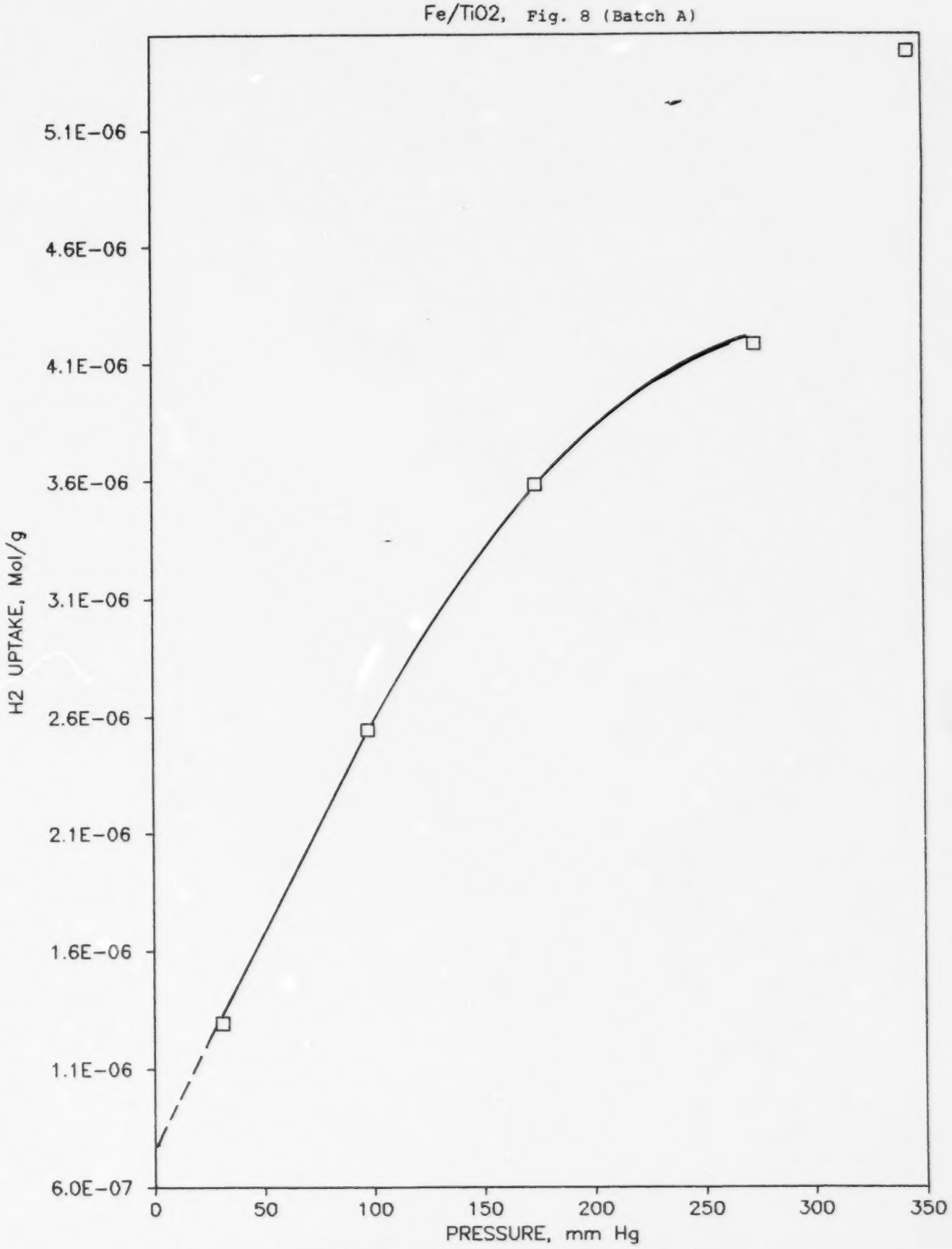

Fig. C3 H_2-Uptake of the Iron/Titania Catalyst (Batch A)

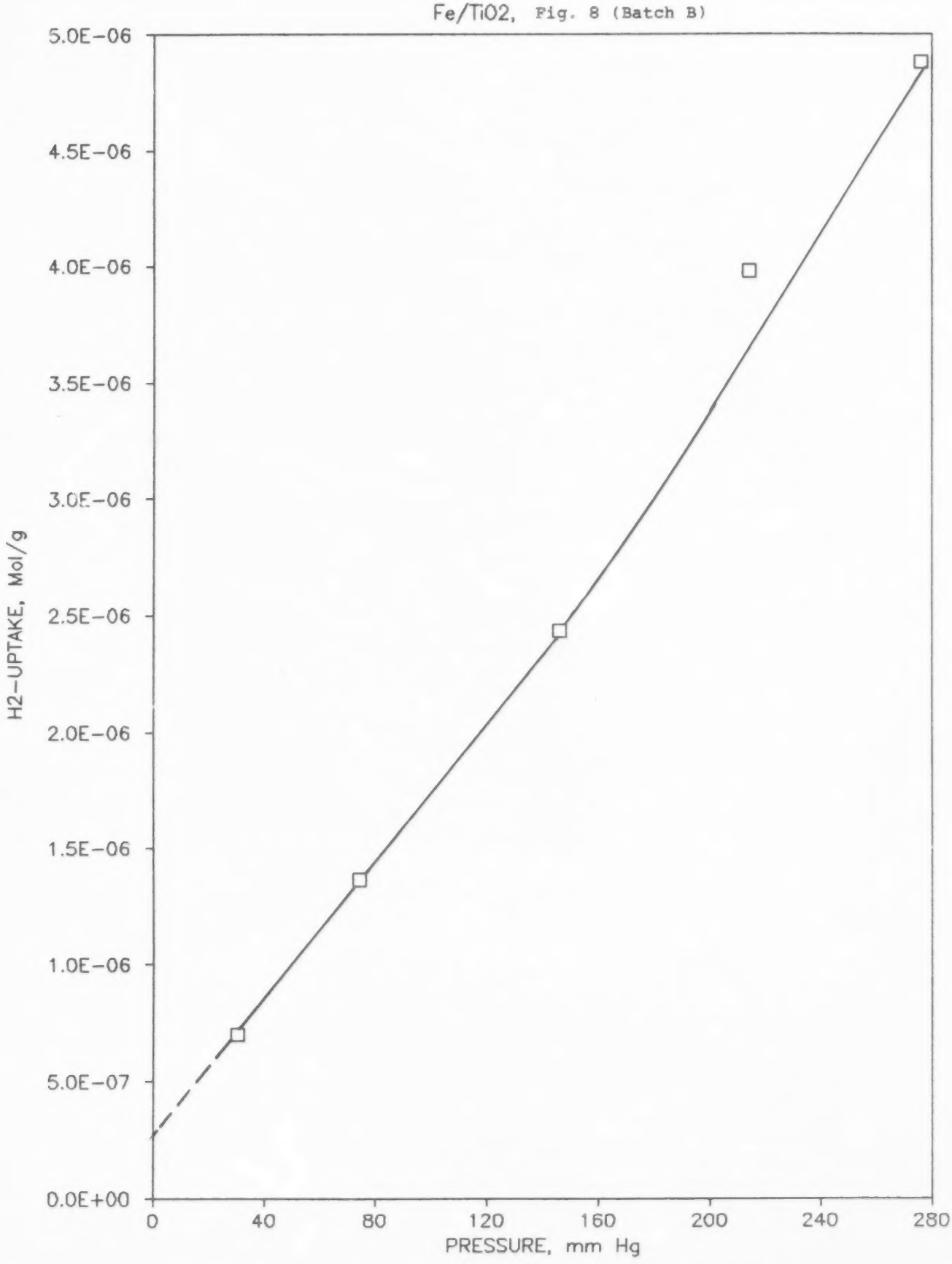

Fig. C4 H_2-Uptake of the Iron/Titania Catalyst (Batch B)

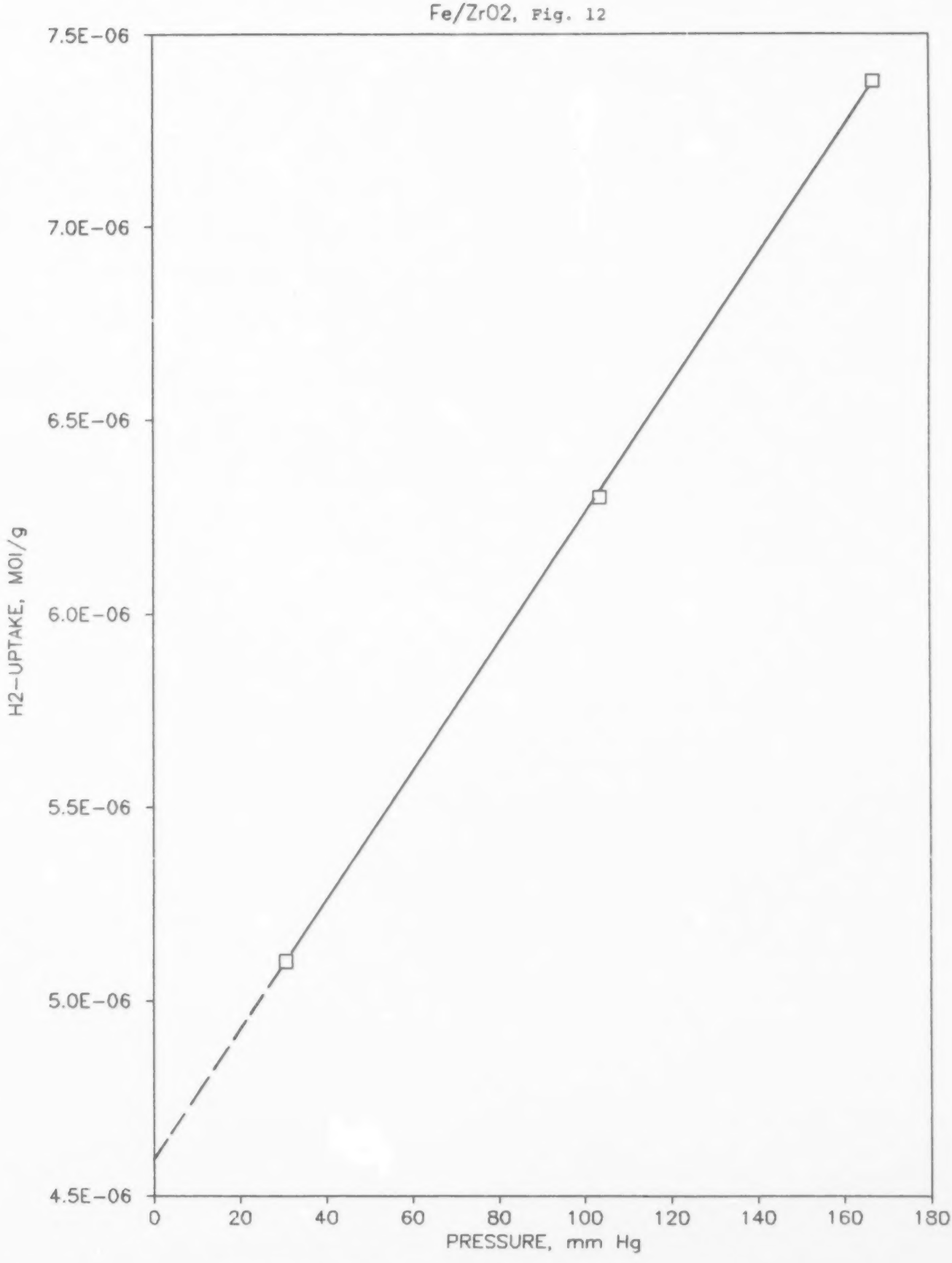

Fig. C5 H_2-Uptake of the Iron/Zirconia Catalyst

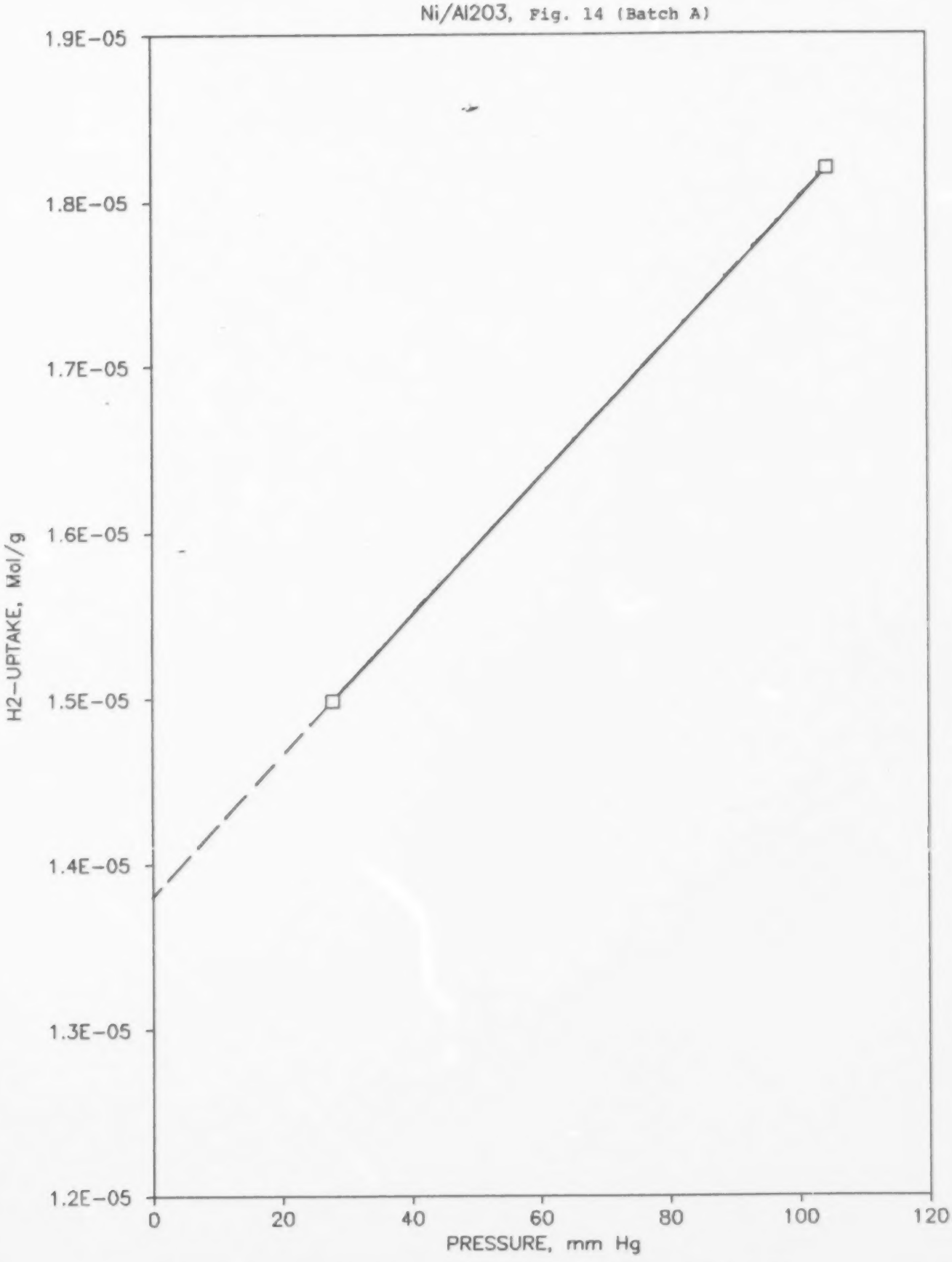

Fig. C6 H_2-Uptake of the Nickel/Alumina Catalyst (Batch A)

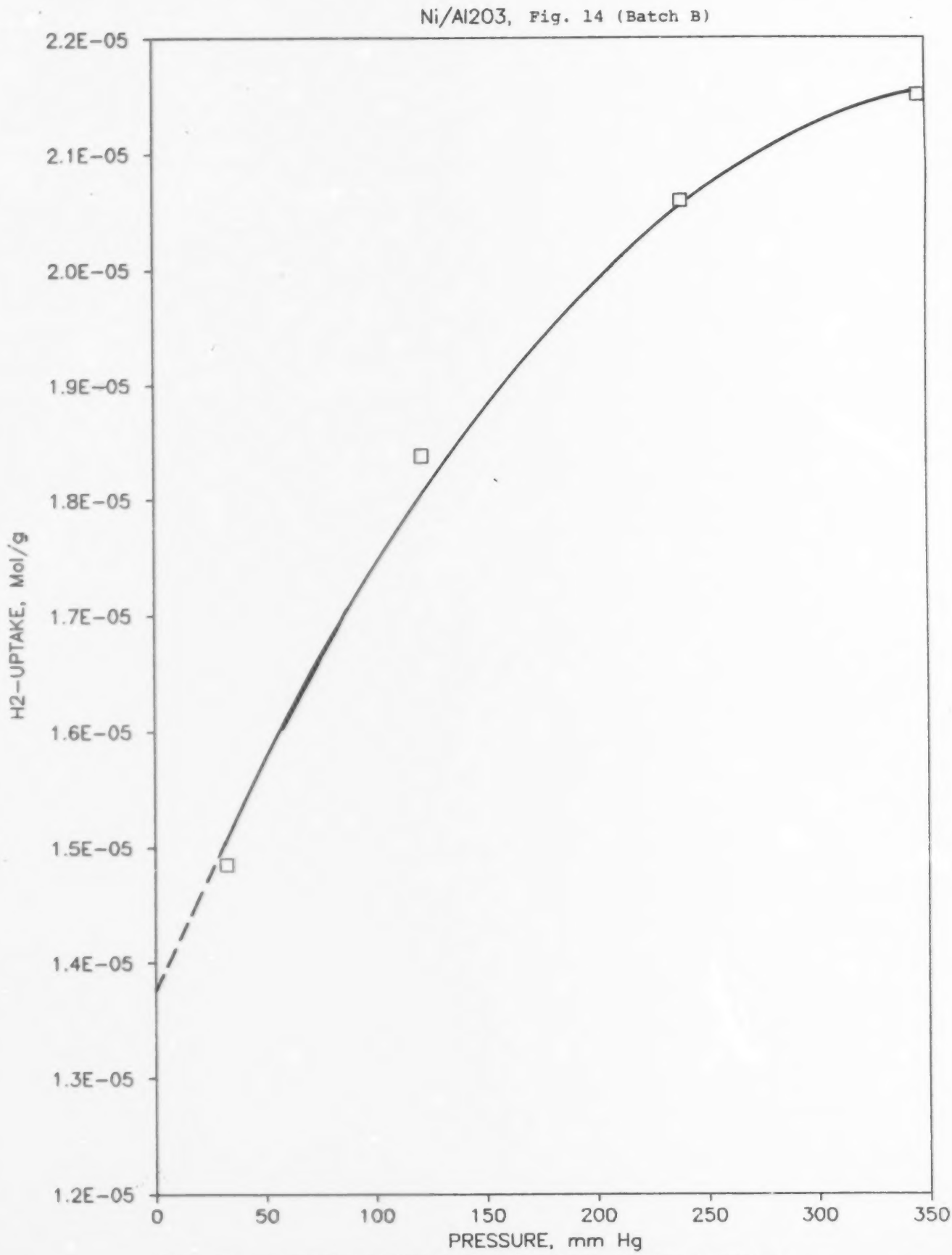

Fig. C7 H_2-Uptake of the Nickel/Alumina Catalyst (Batch B)

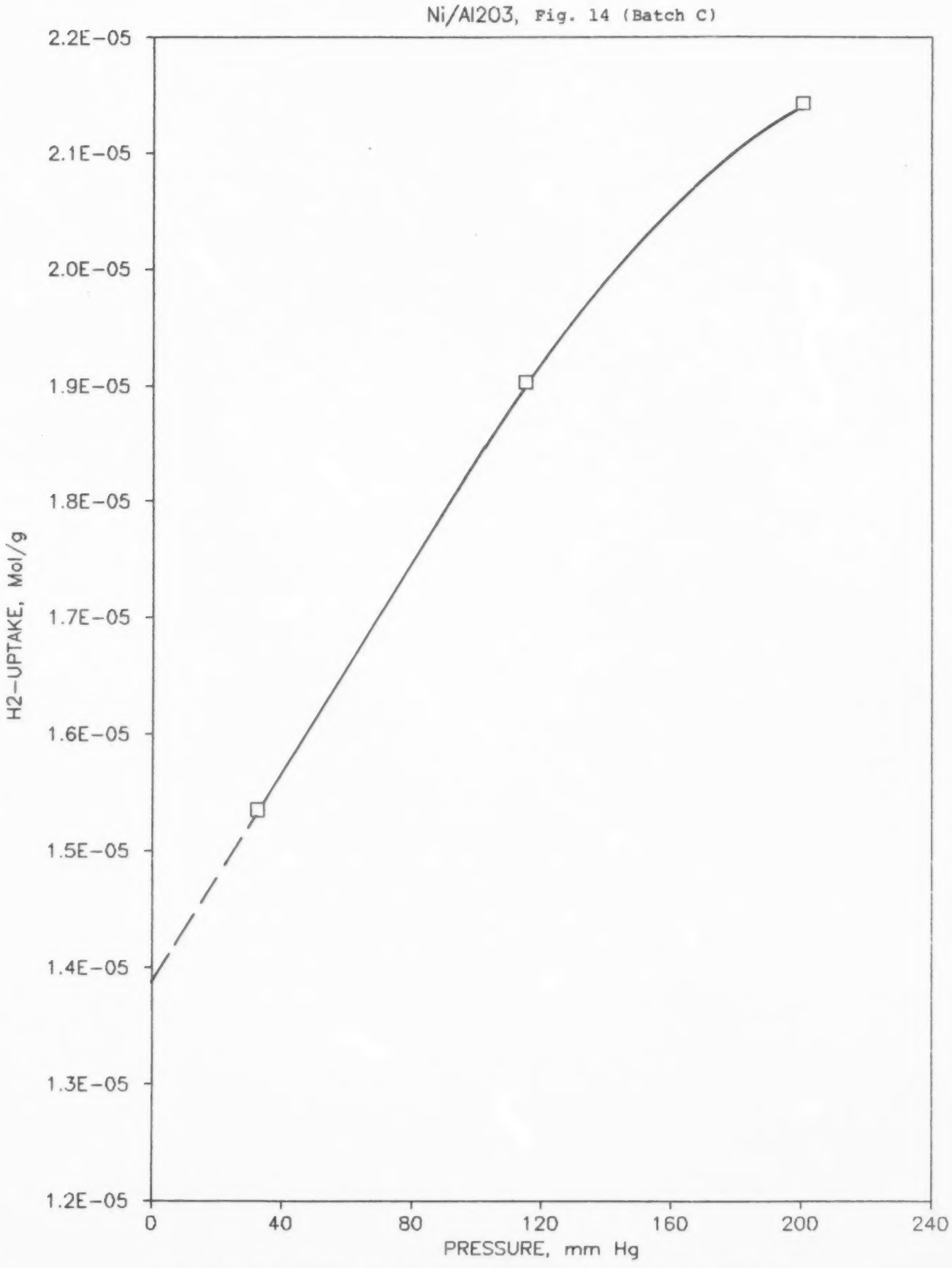

Fig. C8 H_2-Uptake of the Nickel/Alumina Catalyst (Batch C)

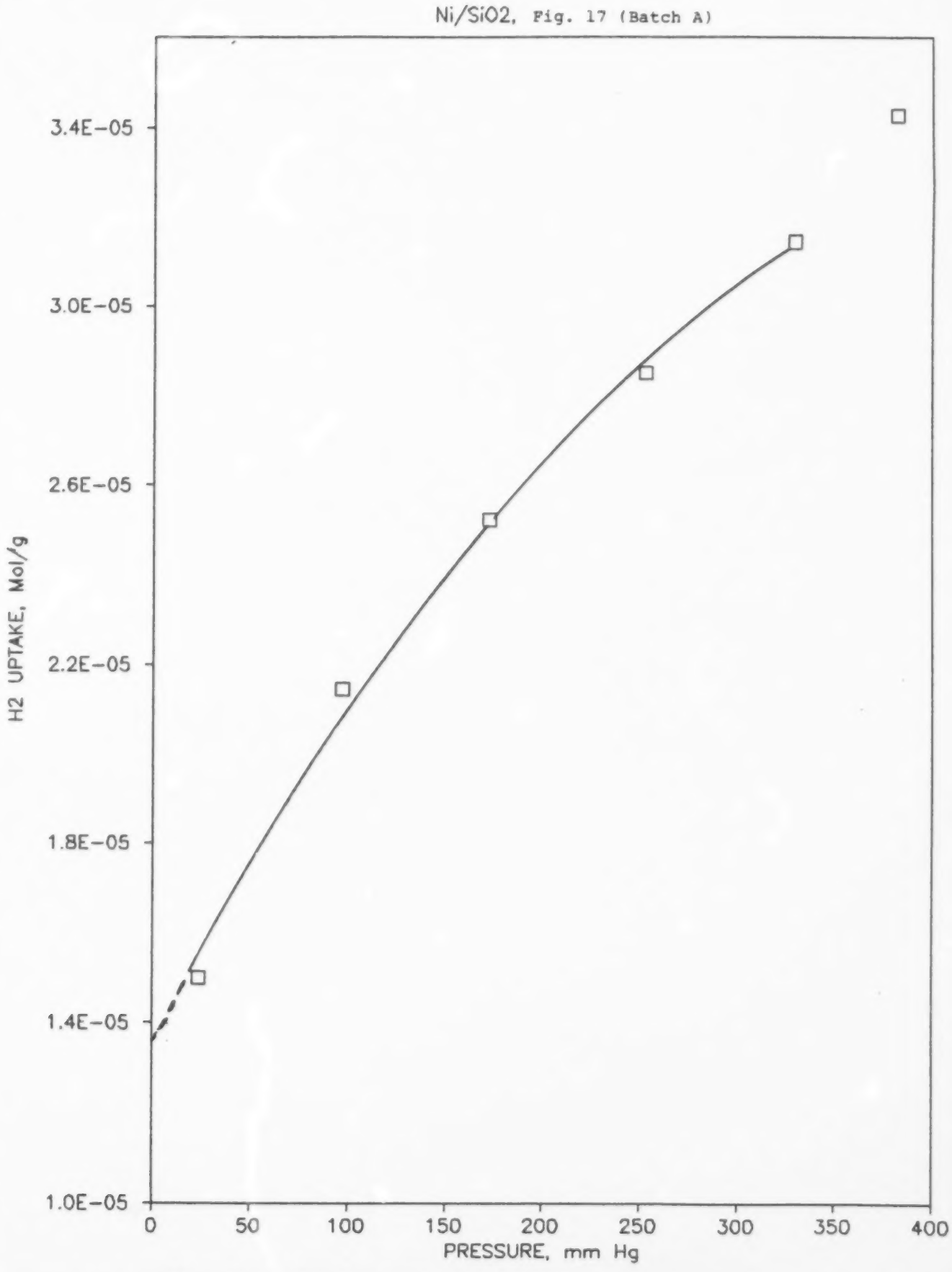

Fig. C9 H_2-Uptake of the Nickel/Silica Catalyst (Batch A)

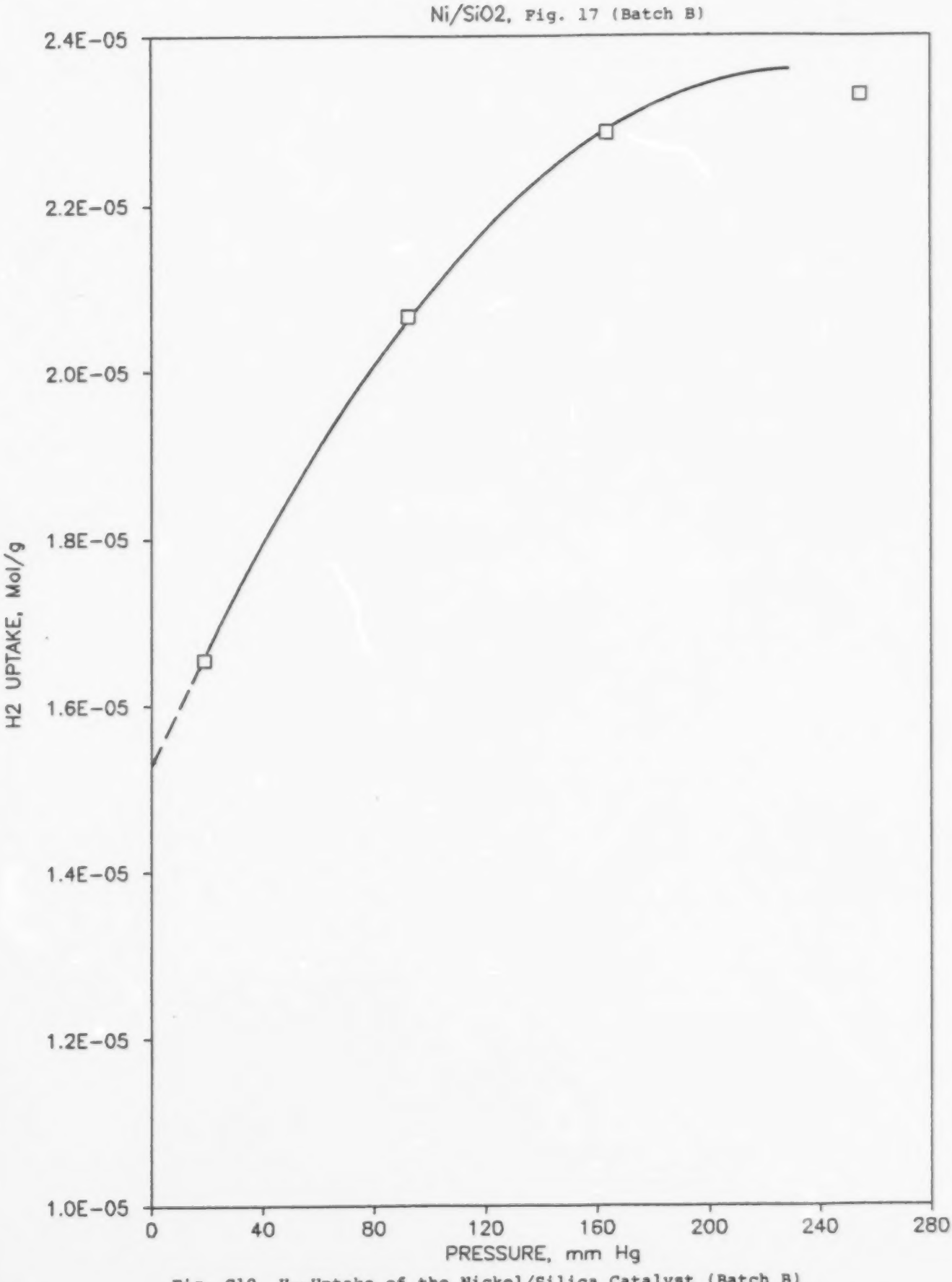

Fig. C10 H_2-Uptake of the Nickel/Silica Catalyst (Batch B)

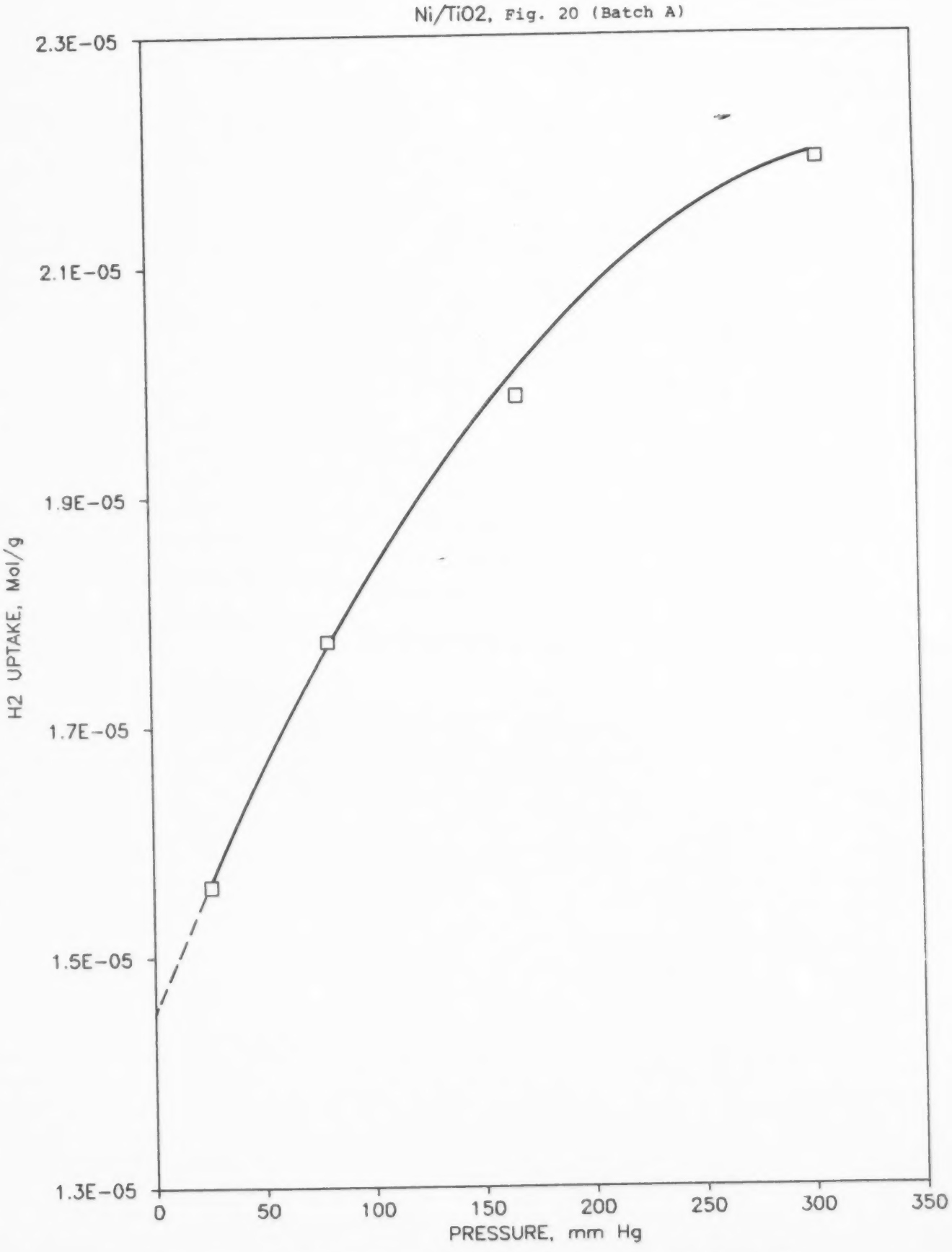

Fig. C11 H_2-Uptake of the Nickel/Titania Catalyst (Batch A)

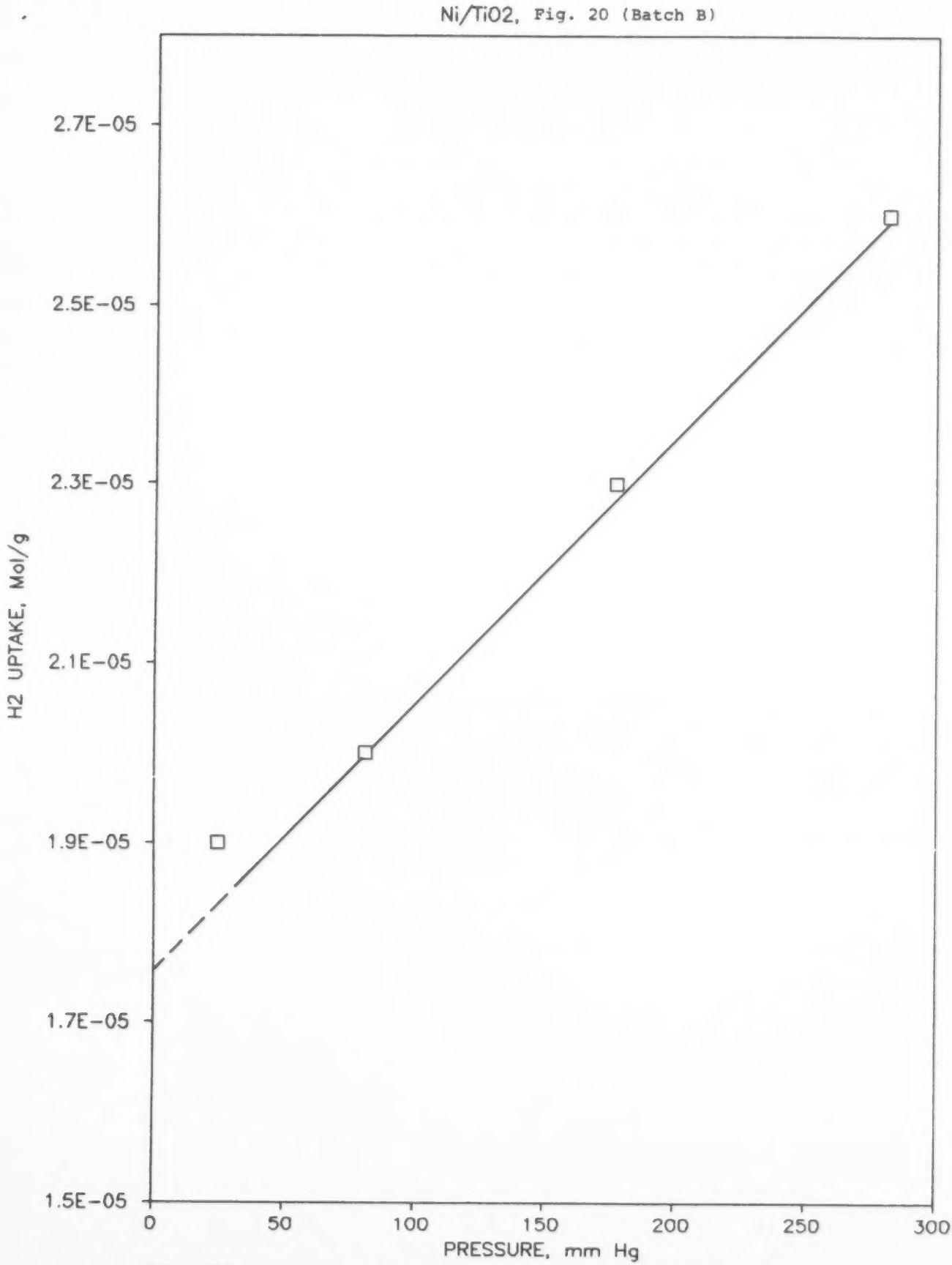

Fig. C12 H_2-Uptake of the Nickel/Titania Catalyst (Batch B)

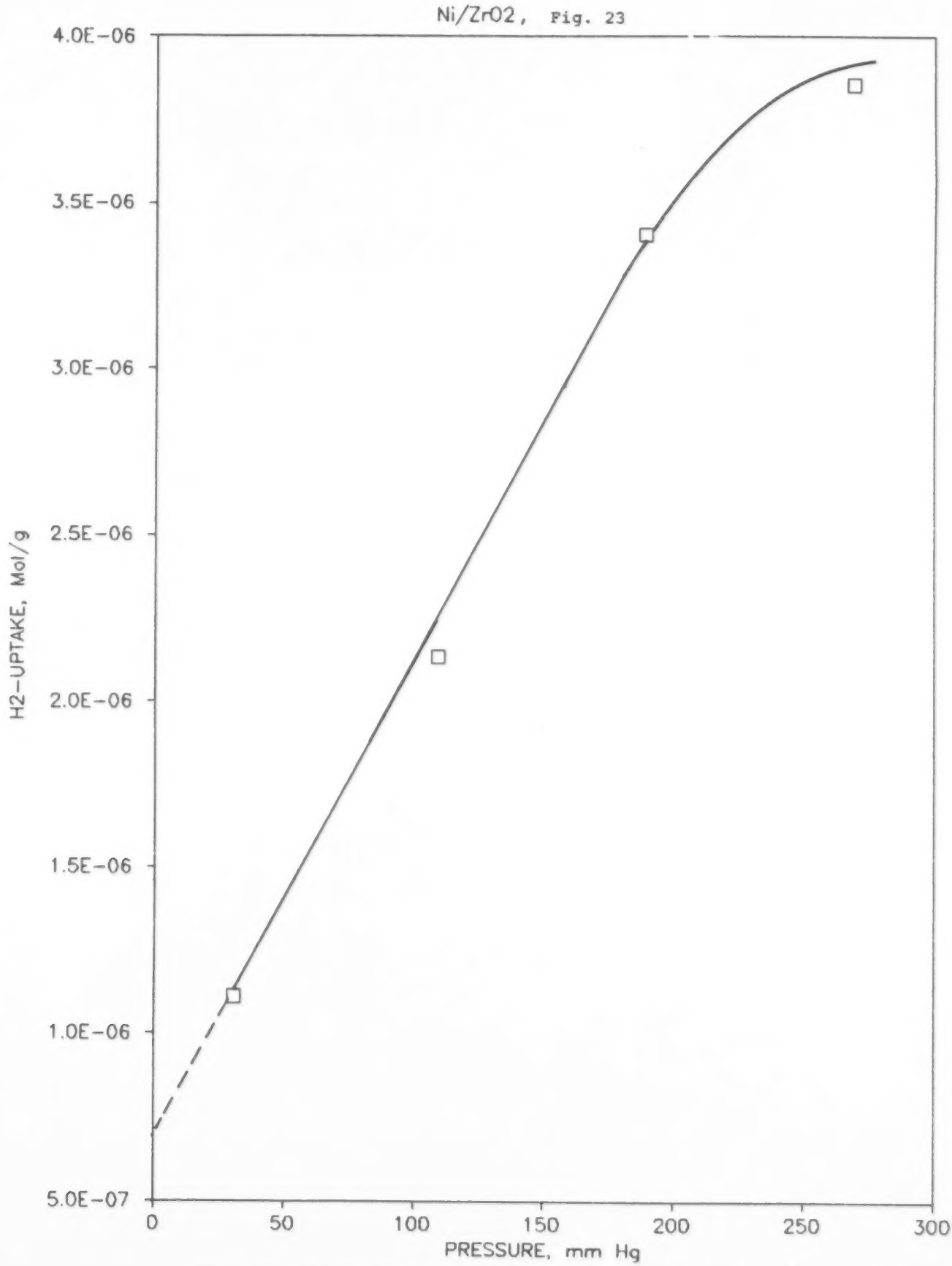

Fig. C13 H_2-Uptake of the Nickel/Zirconia Catalyst

APPENDIX D

Procedures Used For Catalyst Characterization

(a) BET Surface Area

A sample of the finished catalyst was degassed. This was done by heating the sample to 200°C under vacuum overnight. The sample bulb was then placed in a Dewar flask containing liquid nitrogen. At liquid nitrogen temperatures, physical adsorption is promoted and chemisorption is inhibited. The sample was then exposed to measured quantities of nitrogen. The BET adsorption isotherm was obtained by calculating the amount of nitrogen adsorbed at each exposure. From the isotherm, the surface area of the catalyst was calculated.

(b) Pore Volume Distribution

After the above isotherm had been obtained for a given catalyst sample, it was saturated with nitrogen. This ensured that all the pores of the catalyst were filled with nitrogen. The nitrogen pressure surrounding the catalyst was reduced in increments, each time waiting for equilibrium to be established before the pressure was reduced again. The amount of nitrogen desorbed from the catalyst sample at each increment was calculated.

(c) H_2-Uptake at 120°C

A sample of the finished catalyst was reduced in a micro-reactor by heating it to 450°C and passing 30 mL/min of hydrogen over the sample for 16 h. The sample was then cooled to room temperature with hydrogen flow continuing. It was then quickly transferred to a sample bulb where H_2-uptake would take place. The sample was heated, in the bulb, to 400°C and exposed to excess hydrogen for 1 h. This was done to reverse any oxidation that may have taken place in the quick transfer from reactor to the sample bulb at room temperature. The catalyst sample was then degassed at 400°C under a vacuum overnight.

The catalyst sample was then brought to a temperature of 120°C and exposed to measured quantities of hydrogen. A hydrogen uptake isotherm was obtained and the curve extrapolated to 0 mm Hg to obtain the H_2-uptake value.

(d) Chemical Analysis

The Saskatchewan Research Council used standard atomic absorption and gravimetric procedures to measure the chemical composition of the catalyst.